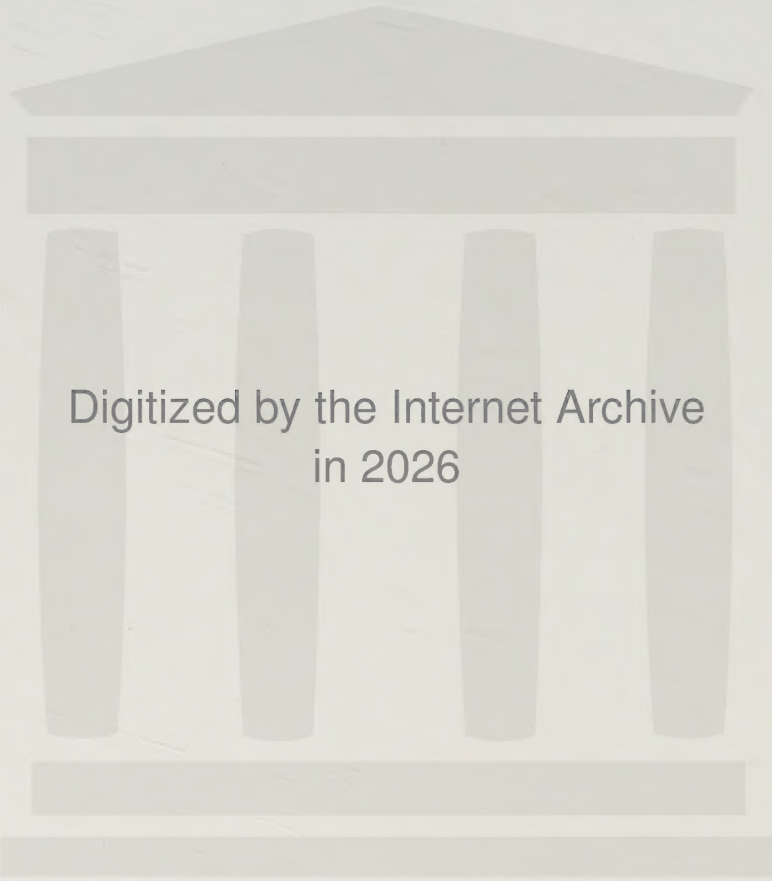


Gunilla Isaksson

STUDIES OF HINDERED INTERNAL
ROTATION IN CONJUGATED SYSTEMS

Lund 1972



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41552414_0059

STUDIES OF HINDERED INTERNAL
ROTATION IN CONJUGATED SYSTEMS.

DISSERTATION

will be publicly discussed in the English language at the
Chemical Center, Lecture Hall A, on January 22nd, 1972,
at 10.15 a.m., for filosofie doktorsexamen (the degree of
Doctor of Philosophy).

by

Gunilla Isaksson, fil. mag., Vrml

Lund 1972



STUDIES OF HINDERED INTERNAL
ROTATION IN CONJUGATED SYSTEMS.

Gunilla Isaksson, fil. mag., Vrml



ACKNOWLEDGEMENTS

I am greatly indebted to my supervisor Professor Jan Sandström for his generous encouragement and continuous interest throughout the work presented in this thesis.

I also wish to thank Professor Salo Gronowitz for his kind interest, and my colleagues and friends for providing a congenial atmosphere in which to work.

Thanks are also due to Mrs. Birgit Dafgård and especially to Miss Heleen Molenaar for help in the preparation of the manuscript. Finally, I wish to thank Mr. Jan Glans for technical assistance and Dr. Robert E. Carter for advice and linguistic criticism.

CONTENTS

SURVEY	1
METHODS	5
Evaluation of rate constants from NMR spectra	5
Dipole moment measurements	11
Ultraviolet spectra	12
Infrared spectra	12
Molecular orbital calculations	12
 PART I.	
<u>para-Substituted N-phenyl-N',N'-dimethylthioureas and</u> <u>para-substituted N-phenyl-N,N',N'-trimethylthioureas</u>	14
NMR measurements	17
Discussion of barriers and chemical shifts	18
Discussion of ultraviolet spectra	27
Molecular orbital calculations	39
On the question of a thione-thiol tautomerism	40
Preparative part	43
 PART II.	
<u>Vinylogous amide and amidine systems</u>	46
Introduction	48
Measurements	49
NMR measurements	49
Ultraviolet spectra	51
PPP calculations	52
Discussion	56
Preparative part	57

PART III.	
<u>Cyclopropanecarboxamide and thioamide</u>	63
NMR measurements	64
Discussion	66
Ultraviolet spectra	68
Preparative part	69
PART IV.	
<u>Substituent nitroethylenes</u>	71
Dipole moments	75
NMR measurements	76
Discussion	81
Ultraviolet spectra	83
PPP calculations	84
Preparative part	87
REFERENCES	91

SURVEY

The work to be described in this thesis concerns the phenomenon of conjugation in organic molecules as studied by NMR measurements, dipole moment determinations, ultraviolet spectra and quantum chemical calculations.

Measurements of the barrier to hindered internal rotation around a bond that is part of a conjugated system provide information about the amount of energy lost by the molecule when the conjugation has been broken. Conjugation alone does not determine the height of the barrier, but steric factors are also of great importance. Steric crowding in the ground state raises the energy and leads to a lower barrier to rotation. On the other hand, steric crowding in the transition state leads to a higher barrier. If the transition state can be stabilized the barrier is lowered.

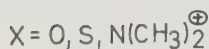
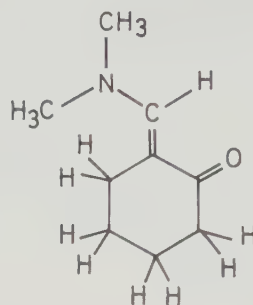
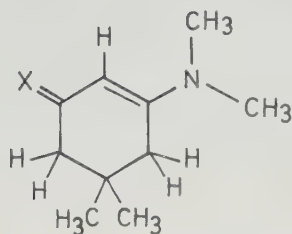
When conjugation increases the charge separation in a molecule, dipole moment measurements give valuable information about the conjugation.

These problems may be approached theoretically by means of quantum chemical calculations. Calculation of the total π -electron energy for the conjugated system minus the π -electron energies obtained from the two parts that arise due to rotation gives the calculated barrier with no steric factors taken into account.

This thesis consists of four parts, the first of which treats hindered internal rotation of the dimethylamino group in *para*-substituted N-phenyl-N',N'-dimethylthioureas and N-phenyl-N,N',N'-trimethylthioureas. A good correlation between the barriers and Hammett's σ -values was obtained. The conformations of N-phenyl-N',N'-dimethylthiourea and N-phenyl-N,N',N'-trimethylthiourea were determined. Information about the conformations was obtained from the chemical shifts of the protons in the aromatic ring and from the concentration - dependent shifts of the methyl groups in the dimethylamino

function at a temperature below coalescence. Furthermore, infrared spectroscopy showed different NH stretching frequencies for Z and E¹ NH groups and ultraviolet spectra provided an estimate of the twist around the carbon-nitrogen bond.

The second part deals with vinylogous amide, thioamide and amidine systems built into rings.



Barriers to rotation around the carbon-nitrogen ($\text{N}-\text{C}$) bonds were determined. PPP calculations could reproduce the results quite well, with one exception. The s-cis conjugated vinylogous amide had a lower barrier experimentally than the s-trans conjugated vinylogous amide but in the calculation the s-cis conjugated vinylogous amide was found to have the higher barrier. The ultraviolet spectra were satisfactorily reproduced in the PPP calculations.

The third part treats *cyclo*-propanecarboxamide and thioamide. The ability of the *cyclo*-propane ring to conjugate with the carbonyl group and the thiocarbonyl group was examined. The *cyclo*-propane ring and the isopropyl group gave the same barrier-lowering effect in the amide case, but in the thio-carbonyl case the *cyclo*-propane ring lowers the barrier more

than the isopropyl group, indicating the better interaction between the *cyclo*-propane ring and the thiocarbonyl group than with the carbonyl group.

The fourth part deals with polarized nitro-ethylenes. The push-pull effect on ethylenes substituted at one carbon atom with a nitro group and at the other carbon atom with alkylthio and/or alkylamino groups lowers the energy of the transition state to rotation around the carbon-carbon bond, thus markedly lowering the barriers. The polarization is examined with the aid of dipole moment measurements as well as chemical shifts and barrier measurements with the NMR technique.

The main part of the results in part 1 and part 3 are published in ref. 2 and 3 respectively.

METHODS

Evaluation of rate constants from NMR spectra.

Many rapid exchange processes with rate constants in the range 10^{-1} - 10^{+5} sec^{-1} can be studied by the NMR technique. The exchange processes cause profound changes in the shape of the NMR signals in this so-called "NMR-time scale".

In the work to be described in this thesis only the two site uncoupled case, A exchanging with B, has been studied.

When the rate of exchange is slow, signals from both of the exchanging sites are obtained, and when the rate of exchange is increased, for example by raising the temperature, the signals broaden and approach each other to give one broad signal at the temperature denoted the coalescence temperature. When the rate constant is further increased the signal sharpens.

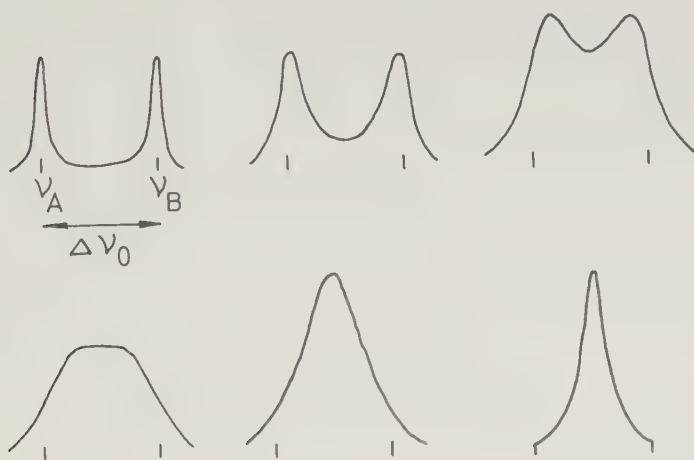


Fig. 1
Pattern of exchange broadening.

The shape of a resonance signal is described by the phenomenological equations of Bloch⁴. When exchange occurs between the two sites A and B, the lineshape of the resonance signal is described by the Bloch equation modified by Gutowsky *et al*⁵ and McConnell⁶, of which the McConnell formulation has been used here. The lineshape of an uncoupled spectrum during exchange is determined by

$$v = \frac{C_1 \left[\left(1 + \frac{\tau}{T_2}\right)P + QR \right]}{P^2 + R^2} \quad (1)$$

where $\tau = \frac{\tau_A \cdot \tau_B}{\tau_A + \tau_B}$

$$P = \tau \left[\left(\frac{1}{T_2}\right)^2 - \Delta\omega^2 + \frac{\Delta\nu_O^2}{4} \right] + \frac{1}{T_2}$$

$$Q = \tau \left[\Delta\omega - \frac{1}{2}(P_A - P_B) \Delta\nu_O \right]$$

$$R = \Delta\omega \left(1 + \frac{2\tau}{T_2}\right) + \frac{1}{2}(P_A - P_B) \Delta\nu_O$$

and C_1 = amplitude factor.

τ_A and τ_B = the mean lifetimes in sites A and B. The exchange

is described by $A \xrightleftharpoons[k_B]{k_A} B$ where $k_A = \frac{1}{\tau_A}$ and $k_B = \frac{1}{\tau_B}$

P_A and P_B = the populations in sites A and B.

$T_2 = T_{2A} = T_{2B}$ = the transverse relaxation time.

$\Delta\nu_O = \nu_A - \nu_B$ = the chemical shift in the slow exchange limit.

$\Delta\omega$ = sweep frequency.

In order to evaluate the mean lifetime two computer programs were used, by means of which the theoretical and experimental lineshapes were compared. In the first program the parameters τ and $\Delta\nu_0$ were varied by hand until the best fit was obtained. In the second program the variable parameters were changed by the program until the best fit was obtained by means of the STEFIT procedure⁷.

Since T_2 and τ are covariant T_2 has been estimated at the pertinent temperatures and given as an input parameter. At temperatures close to and above coalescence, $\Delta\nu_0$ and τ are covariant. By plotting $\Delta\nu_0$ below coalescence vs T and extrapolating to higher temperatures $\Delta\nu_0$ was obtained.

When $P_A = P_B$ and the assumption is made that $\frac{1}{T_{2A}} = \frac{1}{T_{2B}} = 0$ the mean lifetime can be evaluated by approximate methods. Allerhand *et al*⁸ and Drakenberg *et al*⁹ have examined the various methods in some detail. In both of these papers it is stressed that systematic errors may be important, and the use of complete lineshape analysis is recommended.

One of the approximate methods, which has been used in this thesis, is the ratio method of Rogers and Woodbrey¹⁰. At temperatures below coalescence the τ value is given by

$$\tau = \frac{\sqrt{r + \sqrt{r^2 - r}}}{\sqrt{2} \cdot \pi \cdot \Delta\nu_0} \quad (2)$$

where r is the ratio between the maximum and minimum intensities of the resonance signals.

Characteristic for this method is that it gives too low mean lifetimes. The systematic error is less than 10 % where $\tau < 0.05$ sec and $\Delta\nu_0 \approx 20$ Hz.

At the coalescence temperature, where r is unity, τ is given by

$$\tau = \frac{1}{\sqrt{2} \cdot \pi \cdot \Delta\nu_0} \quad (3)$$

T_2 , the transverse relaxation time can be calculated from the relation $T_2 = \frac{1}{\pi \Delta\nu_{\frac{1}{2}}}$, where $\Delta\nu_{\frac{1}{2}}$ is the linewidth of resonance signal at half height. T_2 can only be measured directly at temperatures where no exchange broadening occurs. By measuring T_2 below and above this temperature range, and interpolating for temperatures in between, approximate values of T_2 may be obtained.

Sometimes measurements cannot be made at temperatures low enough to prevent exchange broadening. In such cases a standard, for example TMS, is added to the sample and the halfwidth of the signal from the standard is measured at each temperature. The halfwidth of the signals from both the exchanging protons and the standard are measured at a temperature where no exchange broadening occurs. The changes due to viscosity and differences in inhomogeneity are shown in the linewidth of the standard. To obtain the T_2 for the exchanging protons at temperature T , the following relation is utilized:

$$\begin{aligned} & \left(\frac{1}{T_2 \text{ exchange}} \right)_T - \left(\frac{1}{T_2 \text{ exchange}} \right)_{\text{high temp.}} = \\ & = \left(\frac{1}{T_2 \text{ standard}} \right)_T - \left(\frac{1}{T_2 \text{ standard}} \right)_{\text{high temp.}} \end{aligned} \quad (4)$$

If the barrier to rotation is higher than 25 kcal/mol the different rotamers can in principle be isolated. In such a case, the rate constants may be simply determined by integration of the signal intensities until equilibrium of the two rotamers is reached.

From the rate constants obtained as described above the following thermodynamic data can be calculated.

The Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303 RT} \quad (5)$$

gives E_a the activation energy, $\log A$ the frequency factor. These parameters can be calculated when rate constants for two or more temperatures are known.

The Eyring equation¹¹

$$\Delta G_T^\ddagger = -2.303 RT \log \frac{h \cdot k}{k_B \cdot T} \quad (6)$$

gives $\Delta G_T^\ddagger$, the free energy of activation at temperature T , which can be calculated when the rate constant at temperature T is known.

From the thermodynamic relation

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

and equation 6, equation 7 is obtained, from which $\Delta H^\ddagger$ and $\Delta S^\ddagger$ can in principle be calculated when rate constants are known for two or more temperatures.

$$\log \frac{k}{T} = \frac{-\Delta H^\ddagger}{2.303 RT} + \log \frac{\kappa \cdot k_B}{h} + \frac{\Delta S^\ddagger}{2.303 R} \quad (7)$$

where

$\Delta H^\ddagger$ = enthalpy of activation

$\Delta S^\ddagger$ = entropy of activation

k_B = Boltzmanns constant

κ = transmission coefficient assumed to be unity

h = Planks constant

Temperature measurements.

The temperature measurements are of great importance for the accuracy of NMR lineshape work. The temperatures can be obtained by means of a capillary containing a solution with at least two signals with a temperature-dependent internal chemical shift. The capillary is centered in the middle of the sample tube by two teflon plugs.

In the beginning of this work the capillaries were calibrated against Varians methanol sample by the substitution method, but Van Geet¹² found deviations when he calibrated Varians methanol sample against a copper-constantan thermocouple. This calibration was repeated, and the Varian sample was found to give temperatures which were too low by 0.9° and 1.6° at -65°C and -34°C , respectively. Corrections were made at temperatures calibrated with the Varian sample, after which all capillaries were calibrated against a copper-constantan thermocouple.

The solutions for the capillaries were chosen so that the exchanging signals and temperature-dependent signals did not overlap.

Various solutions were used: a) neat methanol, b) methanol and hydrochloric acid, c) methylene chloride, methanol- d_4 and hydrochloric acid, d) β -picoline and water.

The shift between the signal from water and that due to the methyl group in β -picoline is more temperature sensitive than the shifts of the other solutions.

The shifts were measured by the sideband technique using a Hewlett-Packard oscillator model 200 CD and a Hewlett-Packard frequency counter model 3734 A.

Apparatus.

The NMR spectra were recorded on a Varian A-60 spectrometer equipped with a Varian V-6031 variable temperature probe and temperature controller. A few spectra were recorded on a Varian XL-100-15 spectrometer. All shifts are given relative to tetramethylsilane as an internal standard.

Dipole moment measurements.

The measurements were made in benzene solutions at 25.0°C. A new bottle of benzene (Merck, zur Analysis) was used. Dibutylether, used as a standard, was freshly distilled.

Apparatus: Dipolmeter, typ DM 01 WTW, GmbH Weilheim Obb. D.

The method of Hedestrand¹³ was used. The dipole moment was calculated by the use of equation 8:

$$\mu^2 = \frac{27 \cdot k \cdot T}{4 \cdot \pi \cdot N_1} \cdot \frac{1}{d_1 (\epsilon_1 + 2)^2} \cdot (a_\epsilon - a_n) \cdot M_2 \quad (8)$$

where

k = Boltzmanns constant

N_1 = Lohschmidts number

d_1 = the density of the solvent

ϵ_1 = the dielectric constant of the solvent

ϵ_{12} = the dielectric constant of the solution

a_{ϵ} = the slope of $(\epsilon_{12} - \epsilon_1)$ plotted against weight per cent of solute.

n_1 = refractive index of the solvent.

n_{12} = refractive index of the solution.

a_n = the slope of $(n_{12}^2 - n_1^2)$ plotted against weight per cent of solute.

M_2 = molecular weight of the solute.

Ultraviolet spectra.

The ultraviolet spectra were recorded on Unicam Model SP 800 and Cary Model 15 recording spectrophotometers.

Heptane, used for ultraviolet spectra, was shaken with conc. sulphuric acid followed by water, dried and distilled through a Vigreux column.

Infrared spectra.

A Perkin-Elmer Model 221 prism-grating instrument thermostated at 25°C was used. The cells consisted of calcium fluoride plates separated by teflon spacers. The cell thicknesses were measured by the interference technique.

Molecular orbital calculations.

The Hückel method.

Some Hückel calculations using the ω -method with β -variation¹⁴ and employing parameter set 4 in ref. 14 were performed.

The Pariser-Parr-Pople method.

The PPP method is a self-consistent LCAO-MO method.

Only the π -electrons are considered according to the π - δ -separation approximation. A good summary of the PPP method is given by Wettermark *et al*¹⁵. The matrix elements in the Fock matrix are

$$F_{\mu\mu} = U_{\mu\mu} + \frac{1}{2} q_{\mu} \gamma_{\mu\mu} + \sum_{\lambda \neq \mu} \gamma_{\mu\lambda} (q_{\lambda} - n_{\lambda})$$

$$F_{\mu\nu} = \beta_{\mu\nu}^{\text{core}} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu}$$

where

$$U_{\mu\mu} = \alpha^{\text{core}}$$

$$\gamma_{\mu\mu} = \text{a one-center repulsion integral}$$

$$\gamma_{\mu\nu} = \text{a two-center repulsion integral}$$

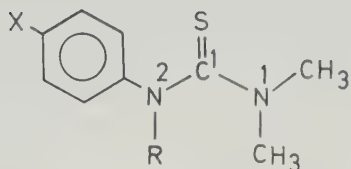
The two-center repulsion integrals are calculated by the Nishimoto-Mataga scheme¹⁶. The PPP method is commonly used for UV calculations, and the parameters are often chosen to give good agreement with UV data. It is also useful for calculating reactivity, dipole moments and barriers to internal rotation.

The program, written by R. Manne at the Quantum Chemical Group, University of Uppsala, is a closed shell π -electron MO-LCAO-SCF program using the method described by Pople¹⁷.

PART I.

para-Substituted N-phenyl-N',N'-dimethylthioureas
and *para*-substituted N-phenyl-N,N',N'-trimethyl-
thioureas.

Attempts to measure the barrier to internal rotation in tetramethylthiourea, as well as that in tetramethylselenourea¹⁸, by the NMR lineshape method have failed, since these compounds give only one signal down to -120°C . This is quite different from other N,N-dimethylthioamides, which have $\Delta G^{\ddagger}$ values for rotation of the dimethylamino group in the range 15-24 kcal/mol¹⁹. In R-CS-N(CH₃)₂, the barrier decreases with



I R=H

a, X=NO₂

b, X=CH₃CO

c, X=CH₃OCO

d, X=Cl

e, X=F

f, X=H

g, X=CH₃

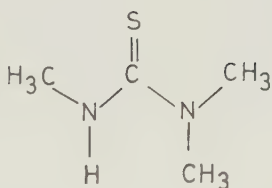
h, X=CH₃O

i, X=(CH₃)₂N

II R=CH₃

a, X=NO₂

b, X=H



III

increasing conjugating capacity of R, and the low barrier of tetramethylthiourea must at least partly be due to the strong electron-donating effect of the dimethylamino group¹⁹. This is supported by the $\Delta G^\ddagger$ value of N,N-dimethyl-N'-acetylthiourea, which is 16.1 kcal/mol¹⁹. However, model studies and also structure investigations²⁰ show that the dimethylamino groups in tetramethylurea and tetramethylthiourea cannot be in the molecular plane, and the steric effect will lower the barrier. The importance of the steric effect is well substantiated by the recent work of Brown and Katekar²¹, who report a $\Delta G^\ddagger$ value of 10.8 kcal/mol for N,N-dibenzyl-N'-methylthiourea. In this molecule planarity is possible.

One would expect the introduction of a phenyl group on one amino group to diminish the conjugating capacity of the nitrogen atom and thereby increase the barrier to rotation of the other amino group, and a preliminary $\Delta G^\ddagger$ value of 11.5 kcal/mol for N,N-dimethyl-N'-phenylthiourea seemed to support this expectation¹⁹. Brown and Katekar²¹ report $\Delta G^\ddagger = 11.3$ kcal/mol for N,N-dibenzyl-N'-phenylthiourea, in agreement with this picture, whereas the value of 10.7 kcal/mol for N,N-dimethyl-N'-phenylthiourea reported by Siddall and Stewart²² seems to be too low.

If the conjugating capacity of the phenyl group is of importance for increasing the barrier, it should be possible to modify its effect by introducing electron-attracting or electron-donating substituents in the *para* position.

The results of an investigation of the barriers in compounds Ia-II and IIa and b are reported. For comparison, N,N',N'-trimethylthiourea III was also studied. The measured barriers are discussed together with other NMR data as well as ultraviolet and infrared spectra with reference to possible conformations of I and II.

NMR measurements.

It was intended to evaluate the rate constants by a complete lineshape treatment. Due to solubility problems the lineshapes have only been studied in rather narrow temperature ranges. Therefore only $\Delta G^\ddagger$ has been reported. Compounds Ie to Ii were measured in deuteriochloroform solutions, but Ia to Id were not sufficiently soluble in this solvent and they were therefore studied in pyridine solution. For comparison, Ie, If, Ih and Ii were studied in the same solvent. Due to signal overlap Ih in pyridine and Ii in both solvents have only been studied at the coalescence temperature by the approximate method using equations 3 and 6. The same applies to IIa and IIb, which were studied in dichlorofluoromethane solution. This solvent is regarded as nearly equivalent to deuteriochloroform in solvating properties. The concentrations employed are found in Table 1. The high concentrations used in pyridine solution were necessary to prevent crystallization. The temperatures were measured by

Table 1. Concentrations of solutions used for lineshape studies.

Compound	Molarity in CDCl_3	Molarity in pyridine
Ia		0.9
Ib		0.9
Ic		0.9
Id		2.6
Ie	0.7	1.8, 1.2
If	0.7	1.9
Ig	0.6	
Ih	0.6	1.9
Ii	0.6	1.8

the concentric capillary technique described above. Where pyridine was used as solvent, methanolic hydrochloric acid was employed in the capillary tubes, but with deuteriochloroform the methanol and sample methyl signals overlapped, and instead a mixture of dichloromethane, concentrated hydrochloric acid and methanol- d_4 was employed. This mixture was unstable and the capillary had to be calibrated in connection with each measurement. The transverse relaxation time was determined as described on page 8. However, this treatment requires that broadening due to longitudinal relaxation can be neglected. That this condition may not always be fulfilled can be inferred from a slightly dissymmetric appearance of the doublets at low temperatures. The high-field N-methyl signal is slightly broader than the other one, possibly due to different relaxation conditions. This effect has also been observed by Siddall and Steward²² in the case of If.

The evaluation of rate constants was performed as described earlier by comparing the experimental curve with a theoretical curve and varying $\Delta\nu_0$ and τ by hand. Above coalescence $\Delta\nu_0$ was not varied.

Discussion of barriers and chemical shifts.

The NMR data, mean life times, τ , and free energies of activation for the rotations are given in Table 2.

A thiourea with negligible steric effects and without extra conjugation was desirable as reference compound, and N,N,N'-trimethylthiourea was chosen for this purpose. In deuteriochloroform at room temperature this compound shows a singlet for the dimethylamino group, whereas the third methyl group appears as a doublet due to coupling with the NH group ($J = 4.6$ Hz). The dimethylamino signal broadens at lower temperatures and splits into a doublet at -62° ($\Delta\nu_0 = 18$ Hz). The resulting $\Delta G^\ddagger = 10.6$ kcal is slightly lower than the value reported for N,N-dibenzyl-N'-methylthiourea²¹.

Table 2. NMR and rate data for I, II, and III.

Compound	Solvent	T K	τ sec	$\Delta G^\ddagger$ kcal/ mol	$\Delta\nu_O$ Hz ^a
Ia	pyridine	222.3	0.0410	11.5	23.0
		223.6	0.0360	11.5	21.6
		224.3	0.0285	11.4	22.2
		225.4	0.0260	11.4	21.2
		225.8	0.0230	11.4	21.6
Ib	pyridine	213.5	0.064	11.2	25.4
		217.6	0.0275	11.1	24.6
		218.2	0.0255	11.0	23.1
		227.0	0.0064	10.9	24.4
Ic	pyridine	210.3	0.0540	10.9	27.8
		215.2	0.0208	10.8	29.4
		220.1	0.0175	11.0	26.2
		229.0	0.0047	10.8	27.8
Id	pyridine	210.1	0.0206	10.5	33.0
		215.7	0.0168	10.7	32.2
		227.0	0.0050	10.8	32.6
		238.1	0.0020	10.9	32.6
Ie	pyridine c = 1.2	215.0	0.0124	10.6	31.4
		228.5	0.0036	10.7	31.4
		236.2	0.00175	10.7	31.4
Ie	pyridine c = 1.8	211.4	0.0222	10.6	32.2
		213.8	0.0193	10.7	32.0
		217.6	0.0136	10.7	30.8
		224.5	0.0064	10.8	31.6
		228.4	0.0034	10.7	31.6
Ie	CDCl ₃	223.0	0.0551	11.6	20.8
		225.3	0.0451	11.7	20.6
		229.5	0.0267	11.7	19.8
		233.7	0.0140	11.6	20.4

Table 2. NMR and rate data for I, II, and III.
(cont'd)

Compound	Solvent	T K	τ sec	$\Delta G^\ddagger$ kcal/ mol	$\Delta\nu_o$ Hz ^a
If	CDCl ₃	217.2	0.088	11.5	27.4
		228.0	0.0344	11.7	26.4
		232.0	0.0227	11.7	25.8
		237.6	0.0080	11.5	26.6
Ig	CDCl ₃	219.3	0.123	11.8	22.0
		224.3	0.0570	11.7	21.2
		228.4	0.0254	11.6	21.2
		232.2	0.0116	11.4	21.6
		237.1	0.0052	11.3	21.6
Ih	CDCl ₃	212.1	0.0810	11.2	21.6
		217.2	0.0614	11.4	21.8
		224.5	0.0317	11.5	22.1
		228.0	0.0184	11.4	21.6
		230.2	0.0171	11.5	20.2
Ih	pyridine	208		10.3 ^b	
Ii	pyridine	205		9.9 ^b	
Ii	CDCl ₃	223		11.1 ^b	
IIa	CHCl ₂ F	170		8.3 ^b	
IIb	CHCl ₂ F	193		9.5 ^b	
III	CDCl ₃	211		10.6 ^b	

^aNon-exchanging chemical shifts, as obtained from the lineshape treatment.

^bBy the approximate method at the coalescence temperature.

It is evident that the $\Delta G^\ddagger$ values of compounds I show no significant temperature dependence within the limits of accuracy of this treatment. This is also in agreement with the trend in recent more accurate studies of hindered rotation in amide-type molecules²³⁻²⁵, according to which the activation entropies are close to zero. In order to make a Hammett correlation the mean values of $\Delta G^\ddagger$ and the Eyring equation⁸ to calculate rate constants for the rotations of compounds Ia to Ii at 223 K were used. The Hammett σ_p -values are taken from the compilation of Jaffé²⁶, except for the value for CO_2CH_3 , which is that given in Ref. 27. Good linear correlations are obtained (Fig. 2), for which ρ -values and regression coefficients

$$\log k = \rho \sigma + \log k_0$$

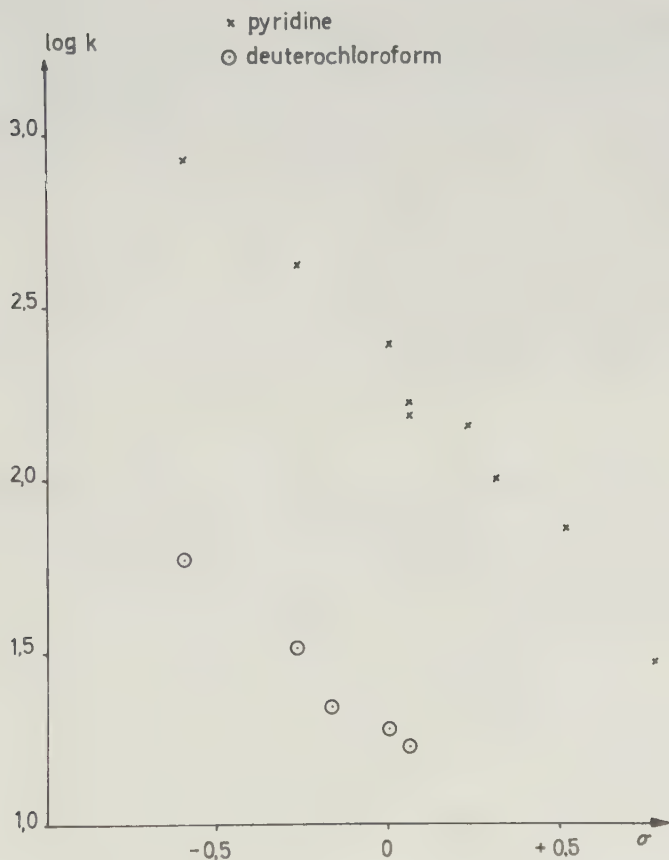


Fig. 2. Hammett correlation for compounds Ia-Ii.

are presented in Table 3. These correlations demonstrate the correctness of the initial assumption of a barrier-increasing conjugation between the aryl group and the thiourea group. The magnitudes of the ρ -values can profitably be compared with the value of - 1.17 calculated from the results of Jackman *et al*²⁸ for the rotation in *para*-substituted N,N-dimethylbenzamides, a reaction with the same electronic requirements as the one studied in the present work. The somewhat lower value obtained here is quite reasonable in view of the greater distance between substituent and reaction center.

Table 3. Hammett correlations for compounds Ia to Ii.

Solvent	ρ^a	R^b	ρ^c	R
CDCl_3	-0.82	0.9858	-0.74	0.9428
Pyridine	-1.04	0.9918	-1.06	0.9787

^aWith all barriers.

^bRegression coefficient.

^cWith the exception of barriers determined at the coalescence temperature only.

The main reason for the lower barriers in pyridine solution is probably hydrogen bonding between pyridine molecules and NH groups, which increases the electron density around the nitrogen atom N² and makes its lone pair electrons more available for a conjugation, which competes with that of the dimethylamino group. This effect will increase the bond order in the C¹-N² bond, thereby increasing the interaction between the aromatic ring and the reaction center, which also explains the more negative ρ -value in pyridine. As will be further discussed in the sections on chemical shifts and infrared spectra, compounds I are partly associated in deuteriochloroform

solution. In order to study the effect of this association on the barriers, a crude coalescence temperature investigation of If in deuteriochloroform at six concentrations in the range 0.06 to 0.76 (molal) has been performed. The coalescence temperature increased by ten degrees in this region, and even if this was partly compensated by an increase in $\Delta\nu_O$, a significant increase in $\Delta G^\ddagger$ with concentration was observed (Table 4). In this case, the result of association is opposite to what was found in pyridine. The effect on the NH group and N² electrons should work in the same direction in both cases.

Table 4. Concentration dependency of $\Delta G^\ddagger$ for If in $CDCl_3$.

c in $CDCl_3$	T_c K	$\Delta\nu_O$ Hz	$\Delta G^\ddagger$ kcal/mol
0.06	222	20.2	11.2
0.12	224	22.6	11.3
0.19	225	24.0	11.3
0.37	228	26.6	11.4
0.56	230	27.8	11.5
0.76	231	30.0	11.5

However, pyridine is a far stronger base than thiourea ($pK_a = 5.17^{29}$ and -1.19^{30} , respectively), and the hydrogen bond and its effect on the barrier should be stronger in the former case. This is also supported by the infrared shifts of the NH band in the two solvents. In deuteriochloroform, the thiocarbonyl group is also involved, and hydrogen bonding will increase the polarity of this group, thereby increasing the mesomeric interaction of the amino groups and thus the barrier.

In compounds IIa and IIb the barriers are about 3 kcal/mol lower than in the corresponding compounds Ia and If. A possible rationalization for this will be discussed in connection with the conformations of I and II.

The chemical shifts of the dimethylamino group (ν_{NMe_2}) in If, IIb, and III have been studied with reference to solvent and concentration effects at room temperature, and

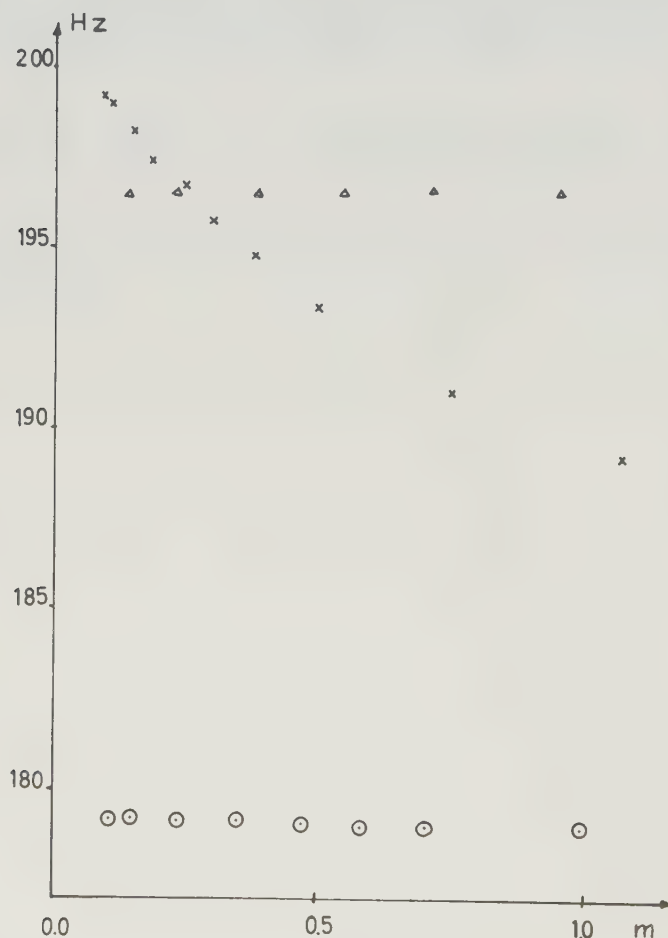


Fig. 3a. ν_{NMe_2} -values for If (x), IIb (o) and III (Δ) in CDCl_3 as function of concentration.

that of If in deuteriochloroform also at temperatures well below coalescence. The ν_{NMe_2} -values of IIb and III show only a small concentration dependence in deuteriochloroform at room temperature, whereas that of If decreases strongly with increasing concentration, its value approaching that of IIb (Fig. 3a). In pyridine, no strong concentration dependence was observed (Fig. 3b), and also in this solvent ν_{NMe_2} was considerably smaller for IIb than for If or III. At a

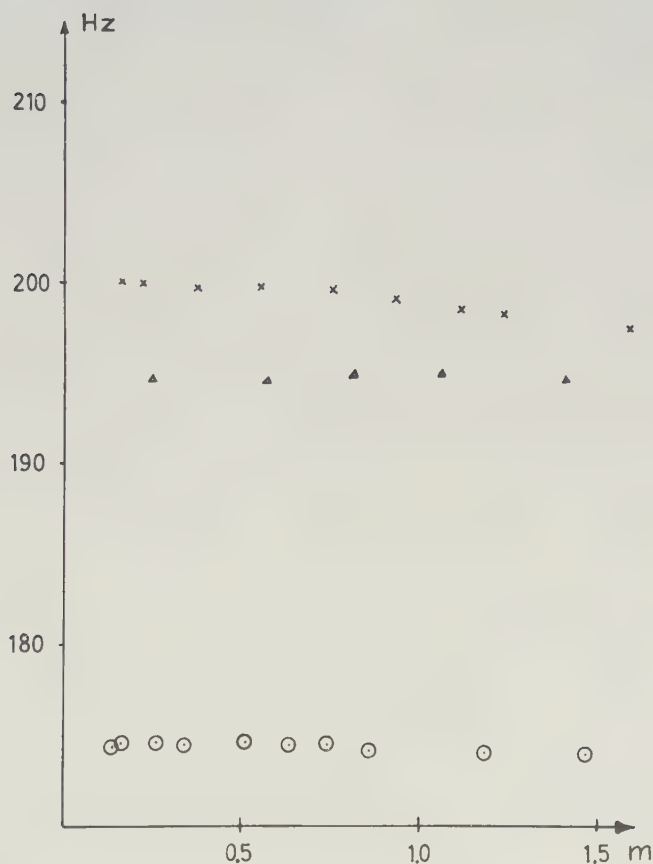


Fig. 3b. ν_{NMe_2} -values for the same compounds in pyridine.

temperature where the rotation of the dimethylamino group was slow (-77°C), both N-methyl signals of If in deuteriochloroform moved upfield with increasing concentration, but the high field signal, which probably comes from the methyl group E to the thiocarbonyl group³¹, showed the largest shifts (Fig. 4).

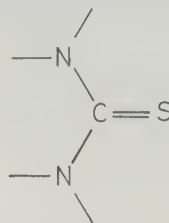
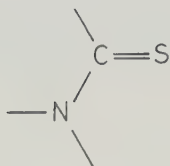


Fig. 4. Chemical shift values for the N-methyl signals of If (below coalescence).

Discussion of ultraviolet spectra.

The ultraviolet spectra are recorded in Tables 5 and 6 together with the spectra of pertinent parent substances.

By means of the LCAO-MO method Janssen³² has calculated the $\pi \rightarrow \pi^*$ transition energies for



which were 1.812β , 1.599β and 1.701β , respectively. This calculation is in good agreement with ultraviolet data on cyclohexanethione, $\lambda_{\max}$ 223 nm³³, thioacetamide, $\lambda_{\max}$ 269 nm and thiourea, $\lambda_{\max}$ 253 nm, all measured in nonpolar solvents.

The ground state polarity of the thiocarbonyl group increases in the series

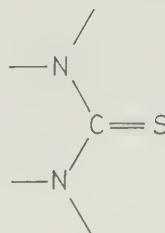
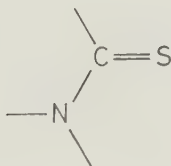
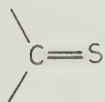


Table 6. Ultraviolet spectra of IIa, IIb, III, Vb, and tetramethylthiourea.

	Hydrocarbons				Ethanol			
	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	Ref.
Trimethylthiourea (III)	251	4.09	295 (Sh)		240	4.14	280 (Sh)	2 32
Tetramethylthiourea	262	4.18	330	2.36	256	4.24	305 (Sh)	2 32
N,N,N'-Trimethyl-N'-phenyl-thiourea (IIb)	274.5	4.27	335	2.66	270	4.30		
N,N,N'-Trimethyl-N'-para-nitrophenyl-thiourea (IIa)	259	3.9	337	4.13	265	4.11	350	4.06
N,N,S-Trimethyl-N'-para-tolyl-isothiourea (VI)	240	4.10	292	3.93				

In the excited state the order of polarities is reversed.

This means that the $\pi-\pi^*$ band undergoes a large blue shift with increasing solvent polarity in thioureas, whereas in thioamides the $\pi \rightarrow \pi^*$ band undergoes a small blueshift with increasing solvent polarity. For tetramethylthiourea the blueshift is smaller than for trimethylthiourea. Trimethylthiourea has a planar structure, but in tetramethylthiourea the methyl groups are too bulky to allow planarity so that at least one of the dimethylamino groups is twisted out of the molecular plane. Tetramethylthiourea has an ultraviolet spectrum and a solvent dependent shift that are more alike the ultraviolet spectra and solvent dependent shifts of thioamides than those quantities of thioureas.

Compounds Ia to Ii display two strong absorption bands in the wavelength region above 240 nm. The long wavelength

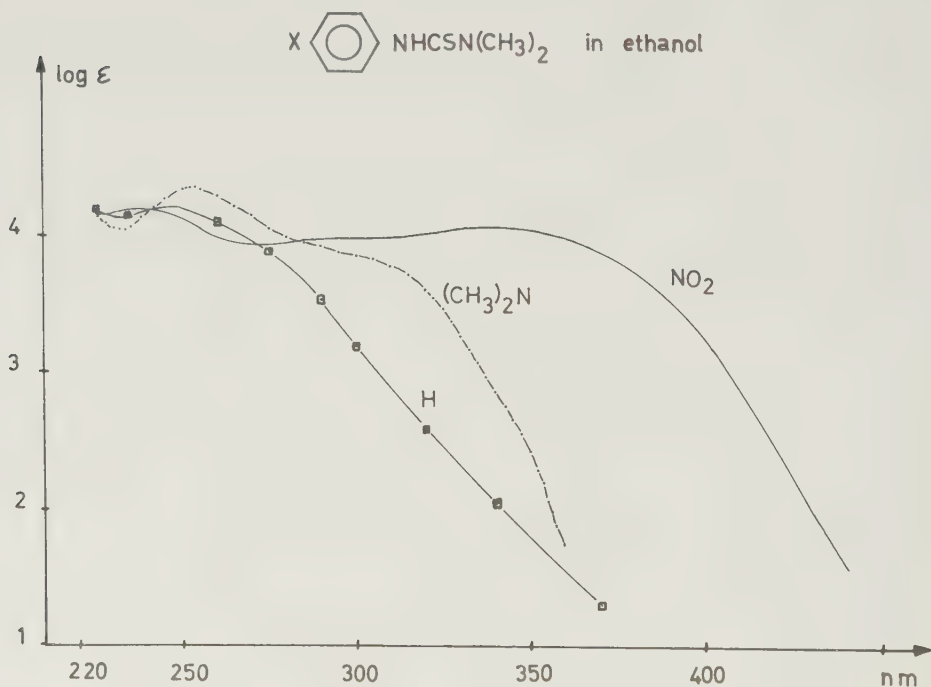


Fig. 5.

band is highly substituent dependent, and in compounds Id to Ii it is only visible as a shoulder. It is shifted to longer wavelengths by substituents with strong + M and - M effect, most strikingly by the latter type (Fig. 5). In Ia, Ib, and Ic the long wavelength band shows a red shift with increasing solvent polarity, which indicates that it is caused by a transition of charge transfer type, localized mainly in the *para*-substituted aniline chromophore. It can be observed that this transition occurs with higher energy in the thioureas than in the free amines, which is reasonable since the lone pair of the amino group is engaged in a conjugation with the thiocarbonyl group, which opposes the charge transfer. The same kind of difference is found between *para*-nitroaniline and its N-acetyl derivative, where the latter has λ_{max} 318 nm ($\log \epsilon = 4.15$) in ethanol³⁴.

In the other compounds of type I, the long wavelength band shows a blue shift with increasing solvent polarity, most pronounced in If, where this band is so strongly displaced that it is completely covered by the second band in ethanol solution. This type of solvent dependence is characteristic of thioureas³².

In heptane solution If shows a weaker band at 325 nm. This undergoes a strong blue shift with increasing solvent polarity, and it is in all probability an $n \rightarrow \pi^*$ band. Its ϵ -value is about ten times higher than in simple thioamides, which can be ascribed to a twisting of the conjugated system. This causes the n and π^* orbitals to mix and removes the prohibition which normally applies to $n \rightarrow \pi^*$ transitions.

The spectrum of IIb shows only one $\pi \rightarrow \pi^*$ band above 240 nm. This band undergoes a blue shift with increasing solvent polarity, but much smaller than that shown by If (Fig. 6). The solvent dependence of IIb is much more similar to that of a simple thioamide. Compound IIb also displays an $n \rightarrow \pi^*$ band in heptane solution.

Compound IIa shows a strong, broad band at 350 nm in ethanol. This band appears at longer wavelength than in Ia,

indicating a stronger *para*-nitroaniline character in the former compound.

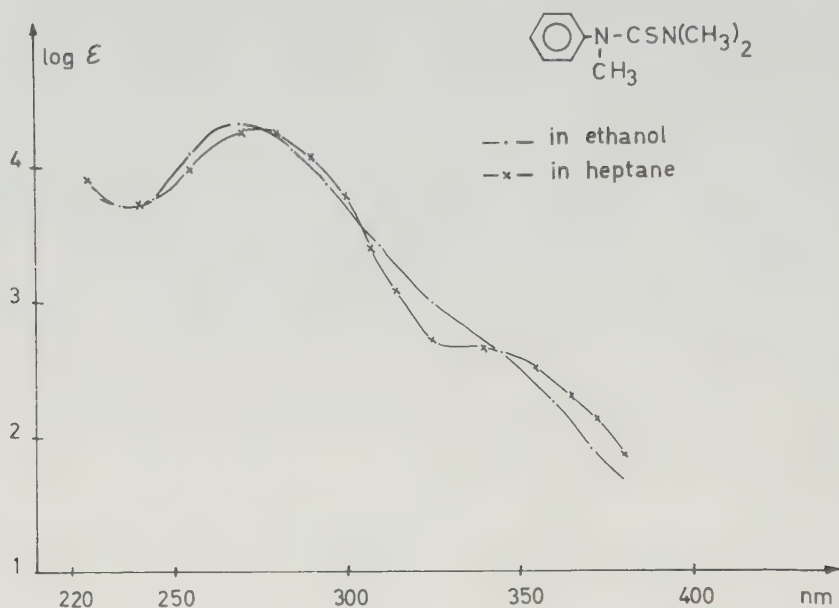


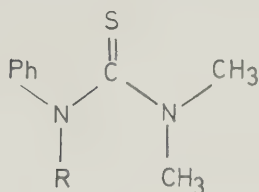
Fig. 6.

Discussion of infrared spectra.

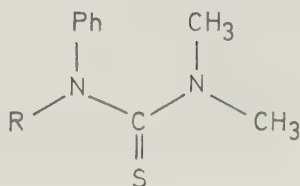
Several authors⁴⁷⁻⁴⁹ have shown that the NH stretching frequency of an amide with the NH and C=O groups in the E configuration is 20-40 cm^{-1} higher than that of the Z isomer. The identification is based on the influence of substituent size on the Z/E ratio, and Siddall *et al*⁴⁹, who isolated pure Z and E isomers of formanilide, which were identified by NMR spectroscopy, could confirm this assignment. Gosavi *et al*⁵⁰ also found two unassociated NH stretching bands in N,N'-dialkyl-

thioureas with alkyl groups large enough to upset the dominance of the conformer with both alkyl groups Z to the thiocarbonyl group.

A quantitative estimation of the different forms requires a knowledge of the ratio of the extinction coefficients of the Z and E monomer NH stretching bands. Russell and Thompson⁴⁷ assumed that these coefficients to a first approximation are equal, and this usage has more or less tacitly been followed by later authors. Recently, Walter and Ruess⁵¹ have shown that If exists in carbon tetrachloride solution ($C = 10^{-3}$) as a mixture of the conformers with the phenyl group Z (A) and E (B) to the thiocarbonyl group in the ratio 1:1.28, with no associated form observable. The two forms are characterized by NH stretching frequencies of 3428 and 3392 cm^{-1} , respectively. In this case, the assignment was confirmed by the influence of *ortho* substituents on the Z/E ratio. Their results were repeated with If and the same two



A



B

R=H or CH_3

adsorption bands were observed, although with a different intensity ratio in deuteriochloroform solution. With increasing concentration, a broad, intense band appears at 3265 cm^{-1} (Fig. 7).

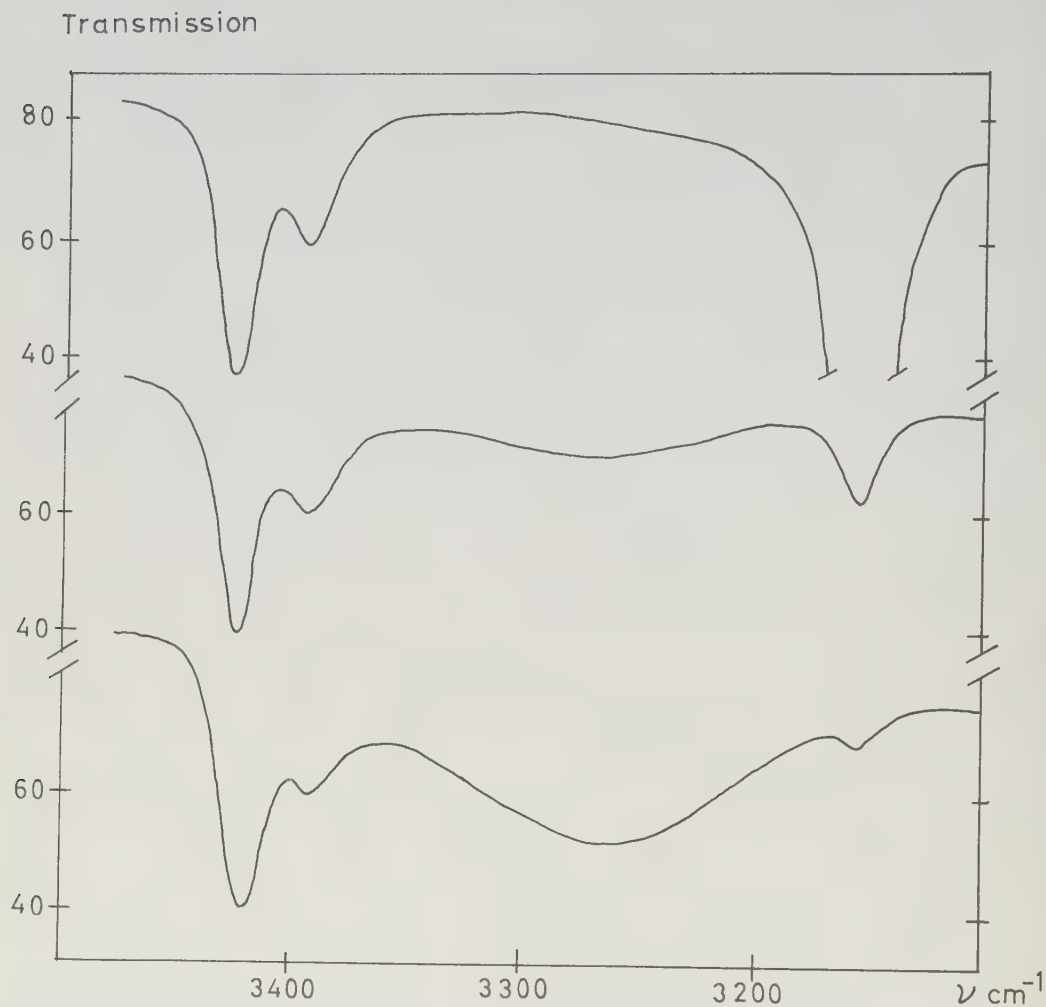


Fig. 7. Infrared spectra of If in 0.04 (cell thickness 0.05 cm, top), 0.4 (0.0056 cm, middle), and 1.0 molar (0.0271 cm, bottom) CDCl_3 solutions. A solvent peak appears at 3155 cm^{-1} .

Three cases have been found where the reliability of the approximation about the extinction coefficients can be tested. According to NMR measurements, N-methylthioformamide exists in various solvents in the form with the methyl group Z to the thiocarbonyl group to the extent of 87-88 %⁵², and from a published infrared spectrum⁵³ a value of 90 % can be calculated for carbon tetrachloride solution. For thioacetanilide in the same solvent, 60 % of the form corresponding to A is obtained from the infrared spectrum⁴⁷, whereas NMR⁵⁴ gives 53.8 %. Walter⁵⁵ has separated the Z and E forms of N-methylthioacetamide and found ϵ -values of 258 and 142, respectively. This indicates the assumption of equal extinction coefficients to be somewhat unreliable. It has been used here only in order to obtain a crude estimate of the isomer ratios.

At low concentrations, where no associated forms were present, the extinction coefficients of form A and B were estimated. These values were then used at higher concentrations to measure the concentration of A and B. The concentration of the associated forms was obtained as the difference

$$C_{\text{total}} - (C_A + C_B) \text{ (Table 7).}$$

In pyridine, no monomer bands are visible. A strong, broad band with maximum at 3225 cm^{-1} must be ascribed to one or more associated forms, whereas a much weaker band at 3125 cm^{-1} may be due to a different type of association or to an overtone or combination band similar to the one found at 3080 cm^{-1} in the spectra of anilides and thioanilides⁴⁸.

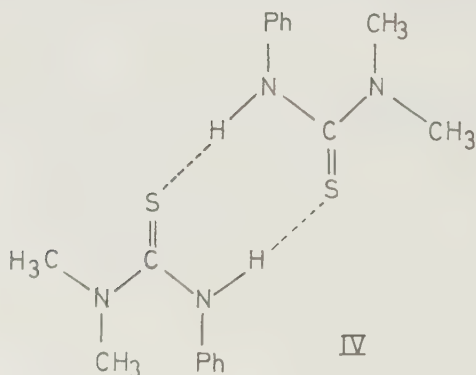
Discussion of the conformations of the N-arylthioureas.

Inspection of molecular models clearly shows that the conjugated systems in I and II cannot be planar, neither in conformation A nor in conformation B, and that the deviations from planarity must be greater in the latter form. As discussed in the section on infrared spectra, If consists of a mixture of monomers of conformations A and B, together with associated

forms at higher concentrations. The dominating conformation among the associated forms can be inferred from the concentration dependence of the chemical shifts of the N-methyl NMR signals of If at temperatures below coalescence (Fig. 4). The large upfield shift of the high-field signal with increasing concentration can only be explained by a conformational change, which places the dimethylamino group, and in particular the methyl group E to the thiocarbonyl group, in a region of stronger shielding. The only reasonable source of strong diamagnetic effects is the benzene ring, and it can be seen on models that the methyl group in question must be situated above the plane of the benzene ring in B (Fig. 8). This change is quite acceptable if the dominant associated form is a dimer, (IV).



Fig. 8. Conformations A and B from Dreiding models.



The small concentration dependence of ν_{NMe_2} for If in pyridine is in agreement with a hydrogen-bonded molecule with a constant Z/E ratio. The large ν_{NMe_2} -value indicates a large proportion of form A (Fig. 3b).

NMR and ultraviolet spectra and studies of molecular models show that the A-B equilibrium must be displaced towards form B in II. As in the associated form of If, the small ν_{NMe_2} -value of IIb is best explained by a large proportion of form²B. It is possible to calculate the shielding effect of the benzene ring in this conformation by the method by Bovey and Johnson⁵⁶, if the geometry of the molecule is known. The shift data tabulated in Appendix B of ref. 57 and several reasonable geometries were used to calculate the difference between ν_{NMe_2} for forms A and B. Values in the range 20-30 Hz (mean for six protons) were obtained, which may be compared with the difference of 22 Hz between the ν_{NMe_2} -values of If and IIb in deuteriochloroform solution, the former extrapolated to zero concentration (Fig 3a). Analysis of the infrared spectra of If in deuteriochloroform shows an A to B ratio of about 3:1 (Table 7), which means that the proportion of B in If at low concentrations is too low to affect the comparison to any great extent.

The non-exchanging chemical shift difference, $\Delta\nu_o$, has been measured for If and IIb in dichlorofluoromethane solution (C about 0.1) below coalescence. The values, 24.6 and 44.0 Hz, are in good agreement with a picture, in which one methyl group in IIb is in a strongly shielded position.

Table 7. Infrared analysis of If in CDCl_3 solution (from spectra in Fig. 7).

Molarity	% A	% B	% associated
0.04	75	25	-
0.4	55	20	25
1.0	45	15	40

The signals of the aromatic protons have not been subjected to a general study. One might expect the thiocarbonyl group to have a deshielding effect on the *ortho* protons in form A. It is therefore of interest to note that the centers of the "doublets" of Ia fall at the 492 and 447 Hz downfield from TMS, whereas those of IIa fall at 492 and 418 Hz, all in deuteriochloroform. The corresponding data in acetone are 490 and 462 Hz for Ia and 490 and 421 Hz for IIa. Rae⁵⁸ has examined the E and Z forms of *para*-nitrothioformanilide in acetone solution. The aromatic protons of the E form give rise to an AA'BB' spectra with the centers of the "doublets" at 500 and 461 Hz. The aromatic protons of the Z form give rise to a singlet that overlaps with the lowfield component of the AA'BB' spectrum of the E form. The shift difference of 39 Hz between the *ortho* protons of the E and Z form is strikingly similar to the shift difference between the *ortho* protons in Ia and IIa, strongly indicating that Ia is mainly form A and IIa mainly form B.

Models show that the phenyl group is subject to stronger steric interferences in form B than in form A, and that these can be relieved by simultaneous rotations around the C¹-N² and N²-aryl bonds (Fig. 8). The importance of the rotation around the C¹-N² bond is shown by the ultraviolet spectra, though these have been recorded in other solvents.

The first $\pi \rightarrow \pi^*$ transitions of Ia, IIa, and *para*-nitroaniline (in ethanol) fall at 339 nm, 350 nm, and 375 nm, respectively (Tables 5 and 6). The larger *para*-nitroaniline character in IIa than in Ia is in agreement with a larger C¹-N² twist in the former and therefore also with a larger proportion of form B. The same conclusion is reached by a comparison of the solvent shifts of If and IIb. The stronger thioamide character of the latter (see discussion of ultraviolet spectra) is in agreement with a larger C¹-N² twist in this compound.

From the available data a picture emerges, according to which form A dominates in dilute solutions of compounds I

in deuteriochloroform, and form B in compounds II under all conditions. The very constant ν_{NMe_2} of IIb in deuteriochloroform solution at different concentrations indicates (Fig. 2a) that the A-B equilibrium in this compound is unaffected by association processes.

The difference of about 3 kcal/mol in the $\text{C}^1\text{-N}^1$ barrier between compounds Ia* and IIa or If and IIb cannot be due to a complete orthogonality between the thiourea group and the benzene ring in II. The barriers of III, 10.6 kcal/mol, and of N,N-dibenzyl-N'-methylthiourea, 10.8 kcal/mol²¹, show that conjugation with the phenyl ring can only raise the barrier by about 1 kcal/mol. Otherwise, orthogonality could be a tempting explanation, since Pedersen⁵⁹ has shown that N-methylacetanilide in the solid state as well as in solution exists almost entirely in the conformation corresponding to B and with the phenyl ring orthogonal to the amide group. On the other hand, acetanilide exists in the conformation corresponding to A, with the benzene ring twisted only about 17° from the amide plane^{60,61}. Furthermore, an orthogonal conformation cannot explain the observation that the increasing effect of a nitro group on the barrier is as large (about 1 kcal/mol) for II as for I. Also, the ultraviolet spectra of IIa and IIb require considerable conjugation through the $\text{N}^2\text{-aryl}$ bond. Instead, the lower barriers in IIa and IIb must be due mainly to the steric strain in the molecule, caused by the methyl group on N^2 . This strain, which originates in interferences with the dimethylamino group in the initial state, is relieved in the transition state, and therefore it serves to lower the barrier, just as proposed for tetramethylthiourea.

Molecular orbital calculations.

In ref. 19 a reasonable linear correlation between $\Delta G^\ddagger$ values and calculated π -electron contributions, ΔE_π , to the

*Corrected to deuteriochloroform solution.

barriers was observed calculation of ΔE_{π} for the N-phenyl thiourea system with the same parameter set has been performed, and a value of 0.496β has been obtained, compared to 0.488β for the simple thiourea system. Both values compare favourably with the experimental barriers of 11.5 kcal/mol for If and 10.8 kcal/mol for III. A least-squares linear correlation line for these compounds and the thioamides in ref. 19 has the equation $\Delta G^{\ddagger} = 80.0 \Delta E_{\pi}/\beta - 27.8$ with a correlation coefficient of 0.933, valid for systems without strong steric interferences.

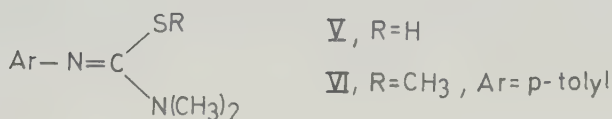
The calculated transition energies for the phenylthiourea system are for the first $\pi \rightarrow \pi^*$ transition 0.995β and for the $n \rightarrow \pi^*$ transition 0.905β . The corresponding values for the simple thiourea system are 1.067β and 0.974β . The ratios between the experimental transition energies, If/III, are 0.923 for the $\pi \rightarrow \pi^*$ and 0.908 for the $n \rightarrow \pi^*$ transition in heptane solution, and the corresponding theoretical ratios are 0.933 and 0.929. Obviously, the effect of the phenyl group is quite satisfactorily reproduced by the calculations.

On the question of a thione-thiol tautomerism.

It could be argued that the difference in rotational barrier between compounds of types I and II is in fact caused by a dominant thiol form (V) in the former group of compounds. Compounds of type V are N,N-dimethyl-N'-arylamidines, and analogous formamidines have shown quite high barriers to rotation around the C^1-N^1 bond^{62,63}. The existence of large proportions of thiol tautomers of different thioamides has been advocated by some authors, but Walter *et al*⁶⁴ have shown that some pyridine carbothioamides are not thiols, as proposed by other authors. Furthermore, Kjellin⁶⁵ has recently measured the thionethiole ratio in thioacetamides and thiobenzamides by the basicity method and found values in the range

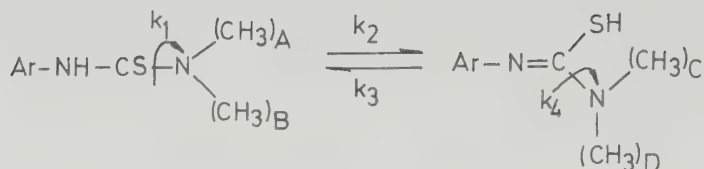
$10^{8.5}-10^{9.6}$, which indicates that the thione form dominates even more strongly in open chain than in cyclic thioamides of the thiopyridone type.

In the present case, the infrared spectra of If in carbon tetrachloride and chloroform solutions show only NH bands and no bands around 2500 cm^{-1} , which could be ascribed to SH stretching vibrations. This at least speaks against a large concentration of thiol form. For comparison the S-methyl derivative of Ig (VI) has been prepared. The ultraviolet



spectrum of this compound (Table 6) is rather different from that of Ig. The maximum of 292 nm in VI has no counterpart in the spectrum of Ig (λ_{max} : 250 nm), and a comparison of the extinction coefficients for the two compounds in the region 290-300 nm shows that at most only a small proportion (less than 10 %) of the thiol form can be present. This argument requires that V and VI have fairly similar absorption spectra, which seems to be a reasonable assumption. Compound VI shows only one signal for the dimethylamino group down to -100°C in carbon disulphide as well as in pyridine-dichloromethane solution. The analogous formamidine has $\Delta G^\ddagger = 14\text{ kcal/mol}^{62}$, and it is obvious that a methylthio group has a similar barrier-lowering effect in amidines as in thioamides, where $\Delta G^\ddagger$ changes from 24.5 kcal/mol for dimethylthioformamide to 15.6 kcal/mol for methyl N,N-dimethyldithiocarbamate¹⁹. The barrier for VI is probably less than 8.5 kcal/mol, since no exchange broadening was visible at -100° . The effect of a possible thiol tautomer on the observed rate constants and

barriers can be discussed, if the exchanging system is treated as a four-site case:



The spectrum will be characterised by four chemical shifts, ν_A to ν_D , four rate constants, k_1 to k_4 , four transverse relaxation times, $T_{2\text{A}}$ to $T_{2\text{D}}$, and the fractional populations P_thione and P_thiol ($P_\text{thione} + P_\text{thiol} = 1$). The lineshape can be calculated from the Bloch equations for the four sites, modified by the appropriate exchanges. If all rate constants are small, four lines will appear at ν_A to ν_D . This is not observed even at low temperatures, which may be due either to a small proportion of thiol form or to the rate constants k_2 and k_3 being large, or to a combination of both. If k_2 and k_3 are large, i.e. if the thione-thiol interconversion is rapid, the observed rate constant, k_obs , will be obtained from the following equations.

$$k_\text{obs} = k_1 \times P_\text{thione} + k_4 \times P_\text{thiol}$$

$$P_\text{thione} \times k_2 = P_\text{thiol} \times k_3$$

In this case, the thiol form can quite well have a considerable influence on k_{obs} even if P_{thiol} is small, provided k_4 is large compared to k_1 , which appears to be the case in the present system. However, this can only lower the barrier, and therefore the presence of a thiol form cannot explain why the barriers of I are higher than those of II. If, on the other hand, k_2 and k_3 are small, the spectrum will consist of two independent exchanging doublets, A-B and C-D, of which only A-B has been observed, and to which the measured rates and barriers apply.

Preparative part.

Compounds Id, Ie, If, Ig and Ii were prepared according to Ho *et al*⁶⁶, by adding a 33 % alcoholic solution of 0.055 mol dimethylamine to a solution of 0.05 mol of the corresponding aniline, 25 ml of ethanol, 0.06 mol of carbon disulphide and 0.00125 mol of sodium hydroxide during 20 minutes at 0-10°C, stirring an additional three hours without cooling and then refluxing twelve hours on a steam bath.

N,N-Dimethyl-N'-anisyl-thiourea (Ih) was prepared using the same method⁶⁶, and a 44 % yield of colourless prisms was obtained, m.p. 126-126.5°. (Found: C 57.8; H 6.29; N 13.2; S 15.1. $\text{C}_{10}\text{H}_{14}\text{N}_2\text{OS}$ (210.30) requires C 57.1; H 6.71; N 13.3; S 15.2).

N,N-Dimethyl-N'-para-nitrophenylthiourea (Ia) was prepared by dissolving *para*-nitroaniline (0.2 mol) in ethanol (600 ml), and adding carbon disulphide (0.72 mol) and N NaOH (15 ml) to the cooled solution. Dimethylamine (0.66 mol) in ethanol (180 ml) was added, and the mixture was refluxed for four days. Even after this time the reaction was far from complete, but the desired product was extracted from unchanged *para*-nitroaniline with N NaOH. On acidification of the alkaline extract, Ia separated as yellow prisms (7 % yield), m.p. 176-177.5° after recrystallization from toluene. (Found:

C 48.3; H 5.02; N 18.8; S 14.1. $C_9H_{11}N_3O_2S$ (225.28) requires C 48.0; H 4.92; N 18.7; S 14.2). Ho *et al*⁶⁶ claim to have prepared this compound but give m.p. 124-125°. Their product is probably a mixture of Ia and much *para*-nitroaniline.

N,N-Dimethyl-N'-*para*-acetylphenyl-thiourea (Ib) was prepared in an analogous way. The crude product consisted of a mixture of Ib and unreacted amine. Extraction of the latter with N HCl gave Ib as yellow prisms (5 % yield), m.p. 167-169° after recrystallization from toluene. (Found: C 59.5; H 6.17; N 12.6; S 14.4 $C_{11}H_{13}N_2OS$ (222.32) requires C 59.5; H 6.35; N 12.6; S 14.4).

N,N-Dimethyl-N'-*para*-carbomethoxyphenyl-thiourea (Ic) was prepared by the standard method of ref. 66 (43 % yield) as colourless prisms, m.p. 175.5-176.5° after recrystallization from toluene. (Found: C 55.4; H 5.78; N 11.9; S 13.5. $C_{11}H_{14}N_2O_2S$ (238.32) requires C 55.4; H 5.92; N 11.8; S 13.5).

N,N,N'-Trimethyl-N'-*para*-nitrophenyl-thiourea (IIa). N,N-Dimethylthiocarbamoyl chloride (8 mmol) and N-methyl-*para*-nitroaniline⁶⁷ (4 mmol) were refluxed in xylene (10 ml) for 12 h. Then triethylamine (8 mmol) was added, and the mixture was refluxed for another 12 h. After cooling, the triethylammonium chloride was removed by filtration, and evaporation of the filtrate gave yellow prisms (35 % yield), m.p. 120-122° after recrystallization from butanol. (Found: C 50.4; H 5.65; N 17.5; S 13.4. $C_{10}H_{13}N_3O_2S$ (239.30) requires C 50.2; H 5.48; N 17.6; S 13.4).

N,N,N'-Trimethyl-N'-phenylthiourea (IIb). N,N-Dimethylthiocarbamoyl chloride (0.012 mol) in benzene was added dropwise to a solution of N-methylaniline (0.024 mol) in benzene (25 ml) and the mixture was refluxed for 24 h. After extraction with water the benzene solution was evaporated, and the solid residue (96 % yield) was recrystallized from heptane to give colourless prisms, m.p. 76-77°. (Found C 62.1; H 7.14;

N 14.4; S 16.6. $C_{10}H_{14}N_2S$ (194.31) requires C 61.8; H 7.26;
N 14.4; S 16.5).

N,N,S-Trimethyl-N'-para-tolyl-isothiourea (VI). Sodium ethoxide (0.05 mol) in absolute ethanol (50 ml) was added to a solution of Ig (0.05 mol) in absolute ethanol (20 ml), followed by methyl iodide (0.05 mol). The reaction was completed at room temperature over night, and the product was vacuum distilled, b.p. $158-160^{\circ}$ at 6 Torr (1.6 g, 15 % yield). The purity was checked by gas chromatography. (Found: C 63.1; H 7.64; N 13.5; S 15.4. $C_{11}H_{16}N_2S$ (208.33) requires C 63.4; H 7.74; N 13.5; S 15.4).

PART II.

Vinylogous amide and amidine systems.

The barrier to rotation about the C-N bond in N,N-dimethylacrylamide has been determined by Kramer and Gompper⁶⁸ to be 15.8 kcal/mol at 308 K. Dahlquist and Forsén⁶⁹ have made a complete lineshape analysis in order to determine the C-N barrier in 3-dimethylamino-5,5-dimethyl-2-*cyclo*-hexenone. They report a $\Delta G^\ddagger$ value of 12.3 kcal/mol at 298 K. Blanchard *et al*⁷⁰ have made lineshape analysis of 1-phenyl-3-dimethylamino-2-propenone and 1-phenyl-3-dimethylamino-2-propenthione, giving $\Delta G^\ddagger$ values of 14.4 and 16.5 kcal/mol at 281 K and 317 K, respectively, for the C-N barrier. Two groups, Filleux-Blanchard *et al*⁷¹ and Dabrowski and Kozerski⁷² have studied 4-dimethylamino-but-3-en-2-one in a mixture of deuteriochloroform and carbon disulphide and in 1,1-dichloroethylene, respectively. NMR spectra at 203 K show the two rotamers, s-trans and s-cis. The NMR spectra are interpreted differently by the two groups of workers. The most reliable assignment of the signals of the two rotamers seems to be that in ref. 72, since the choice made in ref. 71 gives a higher percentage of s-trans form when the substituents at the carbonyl carbon is changed from methyl to isopropyl. Infrared studies of 2,2-dimethyl-5-dimethylaminopent-4-en-3-one, in which the spectra of vinylogous amides in rigid structures are used for comparison⁷³, show that this molecule exists only in the s-cis form.

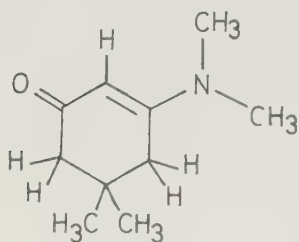
Dabrowski and Kozerski⁷² studied the barrier to rotation around the carbon-carbon single bond in 4-dimethylamino-but-3-en-2-one, and obtained $\Delta G^\ddagger$ values of 11.5 ± 0.2 kcal/mol for s-cis to s-trans and 11.1 ± 0.2 kcal/mol for s-trans to s-cis. The ratio of s-cis/s-trans was 2.52 in 1,1-dichloroethylene at 203 K.

The introduction of a double bond between the carbonyl and dimethylamino groups lowers the barrier to rotation around the carbon-nitrogen bond from $\Delta G^\ddagger = 20.9 \pm 0.1$ kcal/mol for neat N,N-dimethylformamide⁷⁴ to 15.8 kcal/mol for N,N-dimethylaminoacrolein⁶⁸. With two double bonds in conjugation between the carbonyl group and the dimethylamino group the barrier is 13 kcal/mol⁷⁵. The barrier to rotation around the carbon-nitrogen

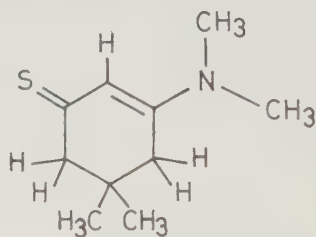
bond decreases as the number of double bonds increases, but with smaller increments for each additional double bond.

Introduction.

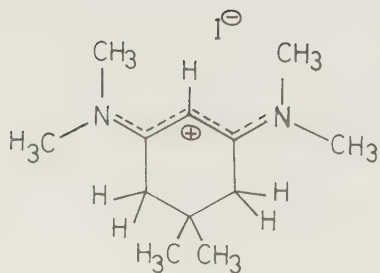
The purpose of this work was to compare vinylogous amides and thioamides in *s*-cis and *s*-trans forms, to see how conjugation in different directions revealed itself in the barrier to rotation around the C-N bond and in ultraviolet spectra, as well as to try to reproduce the results by quantum chemical calculations. In spite of many attempts to synthesize the *s*-cis vinylogous thioamide, this molecule was not obtained. In order to fix the conjugated systems, they were built into six-membered carbon rings. The following compounds were compared:



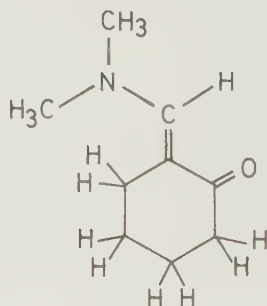
VII



VIII



IX



X

Compound IX was also investigated to obtain a comparison in the series $X = O, S, N(CH_3)_2^{\oplus}$.

MEASUREMENTS.

NMR measurements.

A complete lineshape analysis of 3-dimethylamino-5,5-dimethyl-2-*cyclohexen*-thione (VIII) in deuteriochloroform solution was carried out to determine the barrier around the C-N bond. For comparison with compound VII, which was measured in deuteriomethylene chloride by Dahlquist and Forsén⁶⁹, the latter solvent would have been a better choice. Unfortunately, the non-exchanging chemical shift for the dimethylamino group of compound VIII in methylene chloride was only 3 Hz. Since the two solvents are very similar in most respects, and the non-exchanging shift in deuteriochloroform for VIII is 5.5 Hz, this solvent was used.

The spectra were recorded at 13 different temperatures in a temperature interval of 44 degrees. At each temperature three spectra were automatically digitized and transferred to a punched tape. The transverse relaxation time was obtained as discussed earlier, with TMS as the standard. The value of T_2 calculated in this way, approximate estimates of the mean lifetime τ , the non-exchanging chemical shift $\Delta\nu_O$, and the digitized lineshapes were used as input data for a UNIVAC 1108 computer. The best values below coalescence for τ and $\Delta\nu_O$ were found by the computer by means of the STEPIT procedure⁷. Above coalescence only τ was varied. Since $\Delta\nu_O$ below coalescence showed no definite variation (Table 8), the mean of these values was used for the higher temperatures.

The temperatures were obtained by means of a capillary containing β -picoline and water. The temperature-dependent shift between the methyl and water signals was measured.

Table 8. Results obtained from a lineshape analysis of 3-dimethylamino-5,5-dimethyl-2-cyclohexen-thione (VIII).

T K	$\Delta\nu_O$ Hz	τ sec	T_2 sec	$\Delta G^\ddagger$ kcal/mol
267.5	5.3	0.514	0.328	15.2
273.8	5.2	0.308	0.455	15.3
276.9	5.0	0.291	0.408	15.5
277.5	5.2	0.277	0.353	15.5
283.1	5.4	0.136	0.398	15.4
285.2	5.7	0.108	0.455	15.4
286.9	5.2	0.110	0.431	15.5
292.3	5.3	0.0543	0.507	15.4
294.8	5.3	0.0442	0.483	15.4
297.2	5.3	0.0339	0.500	15.4
301.2	5.3	0.0207	0.442	15.3
308.6	5.3	0.0128	0.507	15.4
311.7	5.3	0.00938	0.500	15.4

$\Delta G^\ddagger$ values were obtained from the Eyring equation (equation 6). The results are listed in Table 8. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from equation 7, which gives $\Delta H^\ddagger = 15.2 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -0.7 \pm 2$ e.u. An Arrhenius plot (equation 5) gives $E_a = 15.8 \pm 0.5$ kcal/mol and a frequency factor of 13.1 ± 0.4 .

The barrier for rotation around the C-N bond in 2-dimethylaminomethylene-cyclohexanone (X) was determined at the coalescence temperature (-83°C) using the approximate formula equation 3. The Eyring equation gave a $\Delta G^\ddagger$ of 9.9 kcal/mol. A mixture of dichlorofluoromethane and pyridine was used as solvent, which gave a non-exchanging chemical shift of 6.6 Hz at -100°C . Other solvents that were tried, *viz.* carbon disulphide and a mixture of methylene chloride and

pyridine, gave no chemical shift of the dimethylamino group at low temperatures. The temperature was measured with a methanol capillary, which was substituted for the sample tube before and after the measurements.

In 1-dimethylamino-3-dimethyliminio-5,5-dimethyl-1-*cyclo*-hexene iodide (IX), the two dimethylamino groups are equivalent, since the positive charge is spread over the whole conjugated system, and the cation has a symmetry plane. The dimethylamino groups give a doublet in the NMR. In deuterio-chloroform solution one of the signals has a shift of 200 Hz and the other one a shift of 202.5 Hz. The resonance signal at 200 Hz is broader and lower than that at 202.5 Hz, probably due to an unresolved coupling with the vinyl proton. All four methyl groups couple with the vinyl proton, but according to the zigzag rule⁷⁶ the methyl groups E to the vinyl proton should show the largest coupling constant, which is apparently not large enough to split the signal at 200 Hz.

At + 60°C the doublet collapsed. At the coalescence temperature, a $\Delta G^\ddagger$ of 18.9 kcal/mol was calculated using equations 3 and 6. The τ value obtained from the NMR curves is for the rotation of two dimethylamino groups. For one dimethylamino group the mean lifetime is twice as large as that obtained from the spectra. This must be taken into account when $\Delta G^\ddagger$ is calculated.

Ultraviolet spectra.

Ultraviolet spectra of compounds VII, VIII, IX and X were recorded in ethanol and heptane or methylene chloride solutions. The results are listed in Table 9. A comparison between N,N-dimethylthioacetamide³², with its $n \rightarrow \pi^*$ band at 365 nm and the first $\pi \rightarrow \pi^*$ band at 272 nm, and compound VIII, with the corresponding bands at 486 nm and 364 nm, shows the influence of a long conjugated system. Ordinary amides do not give any absorption above 205 nm. Compounds X and VII give

$\pi \rightarrow \pi^*$ bands at 305 nm and 280 nm, respectively. Crotonamide, which has the same components in the conjugated system but in cross conjugation, shows no absorption above 205 nm⁷⁷. Most remarkable is the large difference in the first $\pi \rightarrow \pi^*$ transition for compounds X and VII.

Table 9. Ultraviolet spectra.

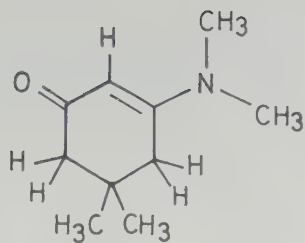
Compounds	$\lambda_{\max}$ nm in nonpolar solvent	log ϵ	$\lambda_{\max}$ nm in ethanol	log ϵ
VII	280 ^b	4.38	298	4.49
VIII	283 ^b	3.14	297	2.75
	364 ^b	4.52	378	4.65
	486 ^b	2.0	-	
IX	328 ^a	4.60	325	4.59
	247 ^a	4.17		
X	305 ^a	4.17	331	4.27

a) in methylene chloride solution

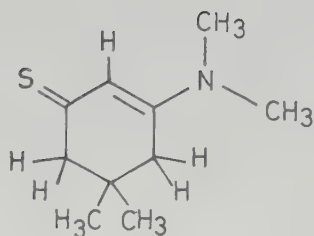
b) in heptane solution

PPP CALCULATIONS.

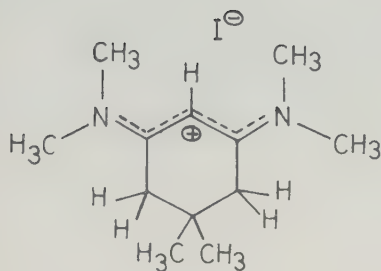
Quantum chemical calculations using the PPP method were carried out on the conjugated parts of the following molecules.



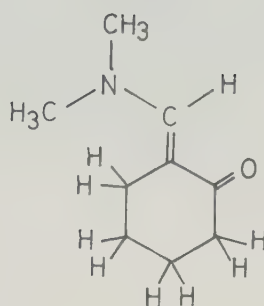
VII



VIII



IX



X

The conjugated systems have fixed geometries since they are parts of rings, and are taken to be planar. An idealized geometry was assumed, with all bond angles to 120° and the bond lengths given in Fig. 9.

For these calculations the parameters were taken from ref. 78. The β -value for sulphur is not given in ref. 78 and has been varied between - 2.0 and - 1.05. The atomic core and one center repulsion integral parameters are from Table 8.4 in ref. 78. In Table 8.5 values for $\frac{\beta}{\beta_s}$ are given. β_s is the value for benzene. A commonly used β_s -value is - 2.32, which was also chosen here. The β -value varies with the bond length. For the carbon-carbon bond, with a length of 1.42 Å, the β -value has been calculated to be - 2.20, and for 1.46 Å to be - 2.07. Mullikan's methods⁷⁹ were used, by which the overlap integral is calculated and from that the β -value.

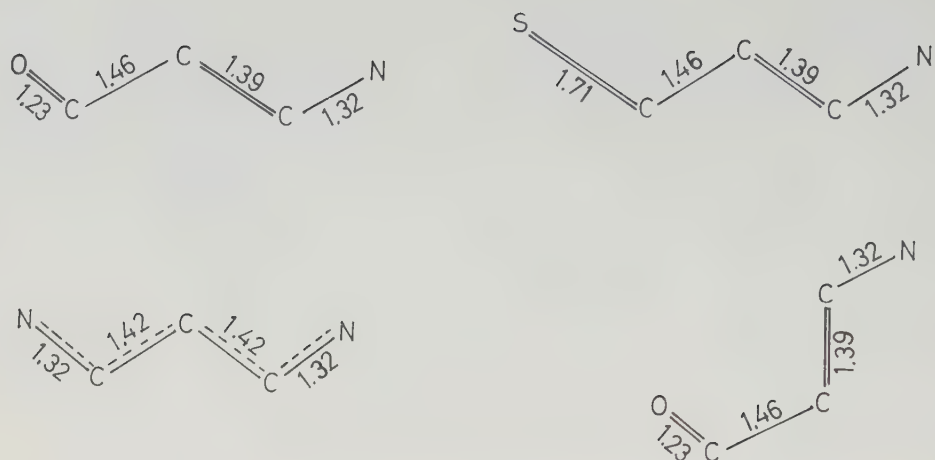


Fig. 9. Bond lengths used in calculations.

Table 10.

	$U_{\mu\mu}$ eV	$\gamma_{\mu\mu}$ eV	$\beta_{\mu\nu}$ eV	bond-length Å
			- 2.32	1.34
$\text{C}-\dot{\text{C}}$	- 11.16	11.13	- 2.26	1.42
			- 2.07	1.46
$\text{C}-\ddot{\text{N}}$	- 28.71	16.75	- 2.0	
$\text{C}-\dot{\text{N}}$	- 14.12	12.34	- 2.46	
$\text{C}-\dot{\text{O}}$	- 17.70	15.23	- 2.27	
$\text{C}-\dot{\text{S}}$	- 12.70	9.94	- 1.05	

The β -value for the carbon-nitrogen bond was varied between - 2.00 and - 1.05. The best agreement with experimental values was obtained with $\beta_{\text{CN}} = - 2.0$.

For the calculations of the conjugated part of compound IX the two nitrogen atoms were considered equal. The β -value for the C-N bonds was chosen to be - 2.2, an average value of - 2.46 and - 2.0.

The barrier to rotation around the carbon-nitrogen bond was obtained as the difference between the total π -electron energy for the whole system and the total π -electron energy when the β -value for the carbon nitrogen bond is zero.

The calculated results, together with the experimental barriers, are reported in Table 11.

Table 11.

Compounds	Calculated ΔE_{π} kcal/mol	Experimental $\Delta G^{\ddagger}$ kcal/mol
VII	16.69	12.3
VIII	17.47	15.5
IX	32.12	18.9
X	18.11	9.9

The ultraviolet spectra were calculated using the same parameters. The results of the calculations together with the experimental results are listed in Table 12.

The ground state energies obtained from the calculations are - 153.24 eV for the s-trans form and - 150.72 eV for the s-cis form. Corrections for the fact that the core repulsions are counted twice give - 96.65 eV for the s-trans form and - 96.08 eV for the s-cis form. The correction terms are

Table 12.

Compounds	Calculated		Experimental	
	$\lambda_{\max}$ nm	oscillator strength	$\lambda_{\max}$ nm	oscillator strength
VII	258.8	0.535	280 ^b	0.393
VIII	227.9	0.067	283 ^b	0.226
	305.9	0.726	364 ^b	0.405
IX	298.5	0.641	328 ^a	0.507
X	277.8	0.428	305 ^b	0.293

a) in methylene chloride solution

b) in heptane solution

different since the geometries are different. The lower calculated ground state energy of the s-trans form, qualitatively is in accordance with the experimental report⁷¹, that 3-dimethylaminoprop-2-enone exists exclusively in the s-trans form. However, the measurements of Dabrowski and Kozerski⁷² indicate that the s-cis form of 4-dimethylamino-but-3-en-2-one in 1,1-dichloroethane is the most stable form.

Discussion.

The entropy of activation for the hindered rotation of the dimethylamino group in VIII is around zero (-0.7 ± 2 e.u.). This is in accord with entropies of activation reported for simple amides⁸⁰. Dahlquist and Forsén⁶⁹ have made a careful investigation of VII. The value for the entropy of activation was 13.23 ± 3 and 13.89 ± 3 e.u. when the measurements were made at 60 and 100 MHz, respectively. The discrepancy in entropy of activation for VII and VIII is difficult to explain. The difference in dipole moment between the ground and transition

states, leading to large difference in solvation, may be a good explanation for the large positive entropy of VII. If this is correct an even larger positive entropy should have been expected for VIII, but this is not the case.

The barriers to rotation were quite well reproducible with the PPP calculation. In the series, VII, VIII and IX, the orders of the calculated and measured barriers are the same (Table 11). The experimental difference in $\Delta G^\ddagger$ between compound VII and VIII is 3.2 kcal/mol but the calculated difference is only 0.8 kcal/mol. For compound IX the calculated barrier is very much higher than the experimental one.

Experiment gives a $\Delta G^\ddagger$ value of 12.3 kcal/mol for compound VII, and 9.9 kcal/mol for compound X. This difference is not reproducible with the calculations, where the barrier for compound X is 1.4 kcal/mol higher than that for compound VII. It is difficult to explain this discrepancy. It might be due to the fact that compound VII is part of a six-membered ring containing three sp^2 hybridized carbon atoms while compound X is part of a six-membered ring containing two such carbon atoms, and thus the angles of the two systems are different. Dreiding models of the two molecules show no appreciable steric hindrance for either of them.

The calculations of the ultraviolet spectra gave maxima at shorter wavelength than found experimentally (Table 12). The first $\pi \rightarrow \pi^*$ transitions are in the same order for the calculated and experimental spectra.

Preparative part.

3-Dimethylamino-5,5-dimethyl-2-cyclohexenone (VII) was prepared according to ref. 69. 14 g (0.1 mol) dimedone and 0.11 mol dimethylamine in benzene were heated in an ampoule at 125°C over night. Evaporation gave 12.0 g of crude product that was sublimated. Mp 104°C; literature value⁶⁹ m.p. 103.7 - 104.0°C.

3-Dimethylamino-5,5-dimethyl-2-cyclohexen-thione (VIII) was prepared by dissolving 3.0 g of VII in dioxane and adding 3.0 g of P_2S_5 . The reaction mixture was stirred for one hour at room temperature and then refluxed for 1.5 hours. The solution was filtered warm and the filtrate evaporated. Water was added to the undissolved residue of P_2S_5 , the mixture was filtered after standing for several hours and the water solution extracted with chloroform. After drying, the chloroform solution was evaporated. The two evaporation residues were crystallized from heptane/toluene 1:1 to yield 1.8 g (55 %) red crystals. M.p. 117° . (Found: C 65.3; H 9.22; N 7.59; S 17.6. $C_{10}H_{17}NS$ (183.32) requires C 65.5; H 9.35; N 7.64; S 17.5).

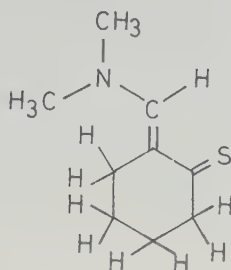
1-Methylthio-3-dimethyliminio-5,5-dimethyl-cyclohexene iodide was prepared by dissolving 0.73 g (0.004 mol) of VIII in 5 ml of abs. acetone. Upon the addition of 0.24 ml methyl iodide, yellow crystals precipitated (1.2 g; 92 %). M.p.: 190° . (Found: C 40.4; H 6.14; I 39.1; N 4.36. $C_{11}H_{20}INS$ (325.26) requires C 40.62; H 6.20; I 39.0; N 4.31).

1-Dimethylamino-3-dimethyliminio-5,5-dimethyl-cyclohexene iodide (IX) was prepared by dissolving 0.4 g (0.00123 mol) of 1-methylthio-3-dimethyliminio-5,5-dimethyl-cyclohexene iodide in 5 ml of chloroform. 0.003 mol of dimethylamine in benzene was added, and the reaction mixture allowed to stand for 12 hours. Benzene was then added and beautiful needles (0.3 g; 76 %) were obtained. They were purified by dissolving in chloroform and adding of benzene. M.p. 185° . (Found: C 44.2; H 6.94; I 39.7; N 8.68. $C_{12}H_{23}IN_2$ (322.24) requires C 44.7; H 7.19; I 39.4; N 8.69).

2-Dimethylaminomethylene-cyclohexanone (X) was prepared according to ref. 73. 22 g (0.19 mol) of hydroxymethylene-cyclohexanone and 0.28 mol of dimethylamine in ether were mixed together. The reaction mixture was allowed to stand for 2 days at room temperature and then refluxed for 2 hours. After drying and evaporation, vacuum distillation gave 22 g (76 %) of a colourless liquid at $140-150^\circ/3$ mm Hg; literature b.p. $97.5/1$ mm Hg⁷³. The substance must be kept under nitrogen in a sealed tube,

as it is unstable at room temperature in contact with atmosphere. The NMR spectrum showed the expected signals.

Attempts to prepare 2-dimethylaminomethylene-cyclohexane-thione.



The usual method for replacing a carbonyl with a thio-carbonyl group is to dissolve the carbonyl compound in a high boiling solvent and then add P₂S₅. Dioxane and toluene are most often good solvents for this purpose, but neither of them led to the desired result. Aliquots were removed after refluxing the reaction mixture for 20, 40 and 60 minutes, but NMR spectra showed that a short reaction time does not change the starting material. When the starting material reacts the dimethylamino group disappears.

The method of Eilingsfeld *et al*⁸¹ in which an amide is reacted with thionylchloride or phosgene to yield an α -chloro-immonium chloride (amidechloride), and the amidechloride subsequently reacted with a nucleophile, (Fig. 10) was also attempted.

To 4.5 g (0.029 mol) 2-dimethylaminomethylene-cyclohexanone in chloroform, 2 ml thionylchloride was added dropwise. A NMR spectrum showed that the amidechloride had formed. When H₂S was bubbled into the solution only polymeric products were obtained. Attempts with sodium hydrosulfide instead of H₂S were also unsuccessful.

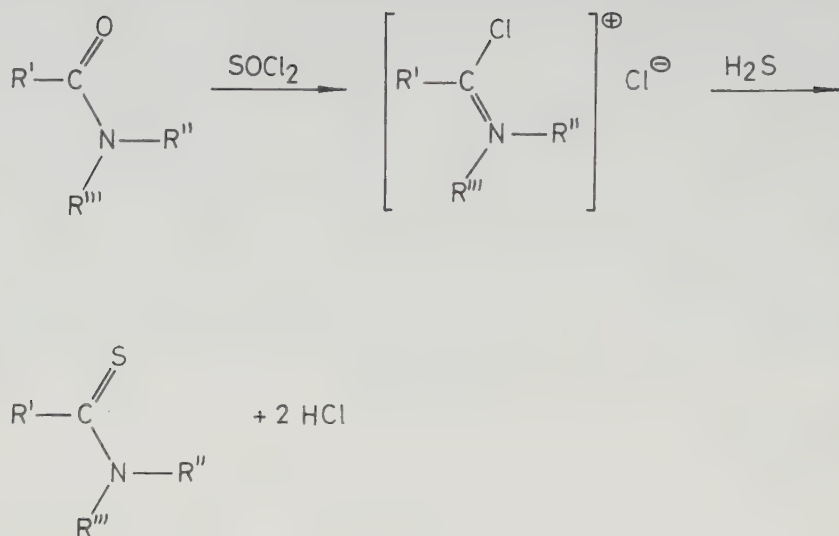


Fig. 10.

The previous results show that the dimethylamino group in this system is labile and for this reason attempts were made to replace oxygen with sulphur prior to the introduction of the dimethylamino group. However, the reaction between P_2S_5 and hydroxymethylene-*cyclohexanon* gave only polymeric material.

An attempt was made to employ a method analogous to that of Lozac'h *et al*⁸², in which 5-phenyl-1,2-dithiolium salt reacts with aniline to give a 1-phenyl-3-aniline-2-propenone (Fig. 11). The corresponding dithiolium salt did not have an aryl group in 5-position, and consequently the ordinary methods of Klingsberg *et al*⁸³ for the preparation of dithiolium salts were useless. Hartman⁸⁴ has synthesized 4,5-tetramethylene-1,2-dithiolium triiodide by methods from ref. 85. He treated an ether solution of 1-formyl-2-chloro-*cyclohexene* and diacetyl disulphide with HI. After 13 hours orange crystals were obtained. M.p. 159-161°. Attempts to react the dithiolium triiodide with dimethylamine using different solvents were unsuccessful.

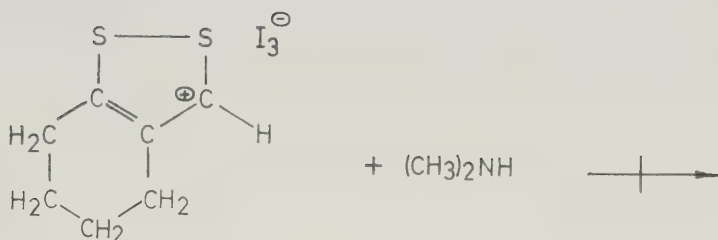
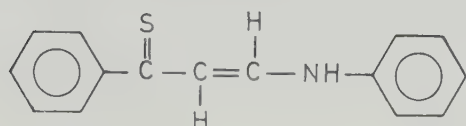
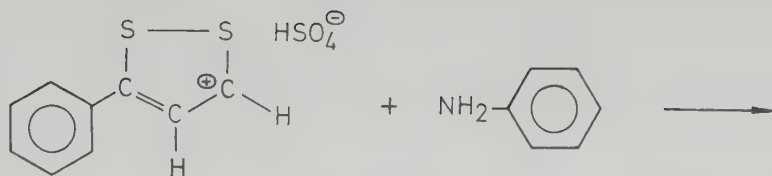


Fig. 11.

Attempts to synthesize 3-dimethylamino-5,5-dimethyl-2-cyclohexene-selenone. 5 g of phosphorous pentaselenide was added to a solution of 5 g of VII in 100 ml of toluene. The reaction mixture was placed in an autoclave and heated to 200°C for three hours. The toluene solution was evaporated and the oil thus obtained was chromatographed on silica gel. The fractions obtained were examined by NMR. The only fraction containing a dimethylamino group was identical with the starting material. In other attempts, with higher temperatures and longer reaction times, no starting material was recovered

but none of the chromatographic fractions gave rise to a dimethylamino signal in NMR.

Attempts to prepare the molecule according to Klayman *et al*⁸⁶ were also carried out. 1-Methylthio-3-dimethyliminio-5,5-dimethyl-cyclohexene iodide was reacted with hydroselenide at pH 8-9. The only defined product obtained was starting material. Different solvent, and different reaction times and temperatures were tried without the desired result. An attempt to make tetramethylselenourea by this method was successful, which shows that the experimental conditions were correct.

One explanation for the failure to prepare the vinylogous seleno compound could be that this molecule is unstable in the presence of mercaptide ions and returns to starting material.

PART III.

Cyclopropanecarboxamide and thioamide.

The ability of the *cyclopropyl* group to conjugate with double bonds is manifested in infrared⁸⁷ and ultraviolet⁸⁸ spectra in dipole moments⁸⁹, as well as in chemical properties⁹⁰. In particular, the conjugation has been found to be effective with positive centra, such as in *cyclopropylmethylcarbonium* ions⁹¹. As previously discussed, (see page 1), the conjugating ability of the group R in R-CX-N(CH₃)₂ (X = O or S) has a considerable influence on the barrier to rotation of the dimethylamino group. For this reason it was considered of interest to measure the barriers in N,N-dimethyl*cyclopropanecarboxamide* (XI) and its thio analogue (XII), and for comparison those in N,N-dimethyl-*isobutyramide* (XIII) and its thio analogue (XIV).

NMR measurements.

For the evaluation of the rate constants from the NMR lineshapes, the ratio method of Rogers and Woodbrey (equation 2) was used for XI and XII. In each experiment the lineshapes were recorded at 10-12 different temperatures. For XIII and XIV, overlap of the N-methyl signals and the methine septet in both cases prevented a study at different temperatures. ν_A , ν_B and the coalescence temperature could be measured and a $\Delta G^\ddagger$ could be determined using equations 3 and 6. *ortho*-Dichlorobenzene was used as solvent in all four cases. Compound XI was also measured neat. With *ortho*-dichlorobenzene as solvent temperatures above room temperature were measured with an ethylene glycol capillary and these below room temperature with a capillary containing acidified methanol. For compound XI without added solvent the amide and methanol methyl signals overlapped. Instead, a capillary containing methylene chloride, methanol-d₄ and hydrochloric acid was utilized. As noted by Carter *et al*⁹² the calibration curve for this type of capillary may change considerably (undergo a parallel displacement) if exposed to high temperatures for a prolonged period of time.

The data obtained are listed in Table 13.

Table 13.

NMR parameters and $\Delta G^\ddagger$ values for
compounds XI, XII, XIII and XIV.

Compound	Solvent	$\Delta\nu_o$ Hz	$\Delta G^\ddagger$ kcal/mol	T_c K
XI	<i>ortho</i> - dichloro- benzene	6.8	16.4 ± 0.4	311.4
XI	neat	17.3	16.1 ± 0.1	319.7
XII	<i>ortho</i> - dichloro- benzene	9.4	18.4 ± 0.3	356.8
XIII	<i>ortho</i> - dichloro- benzene	3.9	16.2	299
XIV	<i>ortho</i> - dichloro- benzene	12.4	19.3	370

(molar fraction of solute = 0.333)

It should be pointed out that in the original paper³ more thermodynamic data were given. Developments in NMR lineshape analysis since the time of the original publication have shown that the approximate methods are insufficiently precise to calculate other than $\Delta G^\ddagger$ values.

Discussion.

It is obvious that steric effects can play an important role in determining the barrier to internal rotation in amides and thioamides. In the ground state, crowding will lower the barrier, while crowding in the transition state will raise the barrier. In the *cyclopropanecarboxamide* and *carbothioamide* the geometry is expected to be similar to that of *cyclopropane-carbaldehyde*. Bartell *et al*⁹³ have shown by electron diffraction that this compound consists of nearly equal amounts of Z and E forms, in both of which the plane of the formyl group bisects the *cyclopropyl* group along its symmetry plane. In this way maximum overlap is obtained between the π -orbitals of the carbonyl group and the carbon-carbon "banana" bonds in the *cyclopropane* ring. In the *dimethylamide* and *thioamide* the Z and E forms are not equally probable. In the conformation in which the (thio)-carbonyl group is Z with respect to the ring, molecular models show that no steric interference exists, but in the E conformation one of the N-methyl groups comes very close to two ring hydrogen atoms. Thus, the molecules have one state which is not crowded, and the measured barrier should be free from large steric effects (Fig. 12).

The effect of conjugation on the barriers can be defined as the difference between the energy of interaction of the substituent R with the (thio)amide group on the one hand and with the (thio)carbonyl group on the other hand. Generally, increasing conjugative capacity of the group R will lower the barrier, since the energy of interaction with the (thio)carbonyl group will be greater than the cross conjugation with the (thio)amide group. The transition state is therefore more stabilized than the ground state by this "extra conjugation". In order to detect possible conjugation with the *cyclopropane* ring comparison may be made with barriers of simple and substituted N,N-dimethylamides and thioamides.

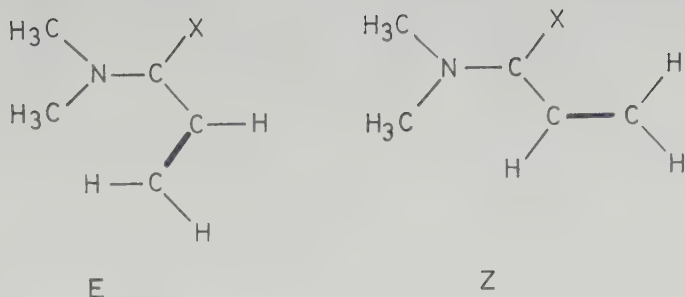


Fig. 12. E and Z form of dimethyl(thio)amide, seen from above the plane bisecting the *cyclopropane* ring. The ring is marked out with a heavier line.

$\Delta G^\ddagger$ for N,N-dimethylformamide has been determined by Drakenberg *et al*⁷¹ to be 20.9 ± 0.1 kcal/mol at 373 K. N,N-Dimethyl-isobutyramide (XIII) has a $\Delta G^\ddagger$ of 16.2 kcal/mol at 299 K and N,N-dimethyl-*cyclopropanecarboxamide* (XI) a $\Delta G^\ddagger$ of 16.4 kcal/mol at 311.4 K.

For comparison to the *cyclopropyl* group the isopropyl group is chosen. This is not a perfect choice, since it is somewhat larger, but it is the best one available. The results show that the *cyclopropyl* and isopropyl groups are about equally barrier lowering.

N,N-Dimethylthioformamide has a $\Delta G^\ddagger$ of 24.0 kcal/mol¹⁹, N,N-dimethyl-isobutyrrthioamide (XIV) a $\Delta G^\ddagger$ of 19.3 kcal/mol at 370 K and N,N-dimethyl-*cyclopropanethiocarboxamide* (XII) a $\Delta G^\ddagger$ of 18.4 kcal/mol at 356.8 K. The *cyclopropyl* group interacts more with the thiocarbonyl group than with the carbonyl group, giving a lower barrier by 1 kcal/mol compared with the isopropyl group.

The specific capacity of the *cyclopropyl* group to stabilize an adjacent positive center⁹¹ does not seem to be of importance here. Molecular orbital calculations by a modified

ω -method¹⁴ show that the π -electron density on the (thio)-carbonyl carbon atom is nearly unchanged when the dimethylamino group is turned out of conjugation.

Ultraviolet spectra.

The carboxamide showed no absorption at wavelengths above 205 nm, which is not surprising since no absorption bands in the near ultraviolet have been reported for acrylamide⁹⁴ or crotonamide⁷⁷.

The carbothioamide, on the other hand, showed a $n \rightarrow \pi^*$ band at 358 nm ($\epsilon = 48$) and a $\pi \rightarrow \pi^*$ band at 277 nm ($\epsilon = 12300$) in heptane. A comparison with N,N-dimethylthioacetamide³², with the $n \rightarrow \pi^*$ band at 365 nm and the $\pi \rightarrow \pi^*$ band at 272 nm, is somewhat confusing since in general both bands undergo red shifts on conjugation⁹⁵. It is of interest, however, that Rogers⁸⁸ has noted similar behaviour for the corresponding bands in the ultraviolet spectrum of *cyclo*propyl methyl ketone.

The charge distribution for S, C, and N in the thioamide group in the ground state, in the $\pi \rightarrow \pi^*$ excited state and in the $n \rightarrow \pi^*$ excited state have been calculated by the HMO method. The results are given in Table 14. They may provide some explanation for the mode of interaction of the *cyclo*-propyl group with the thioamide group. It was mentioned above that conjugation between the *cyclo*-propyl group and a positive center is effective.

The *cyclo*-propyl ring can conjugate better with the $\pi \rightarrow \pi^*$ excited state of the thioamide group than with the $n \rightarrow \pi^*$ excited state of the same group, since the electron densities at the carbon atoms are 1.203 and 1.437, in the respective excited states. That could explain the red shift of the $\pi \rightarrow \pi^*$ band and the blue shift of the $n \rightarrow \pi^*$ band of the *cyclo*propanethioamide compared with N,N-dimethylthioacetamide.

Table 14.

Calculated π electron distribution in
different states of the thioamide group.

State	q_S	q_C	q_N
Ground	1.311	0.874	1.816
$\pi \rightarrow \pi^*$	1.014	1.203	1.783
$n \rightarrow \pi^*$	1.655	1.437	1.908

Preparative part.

N,N-Dimethylcyclopropanecarboxamide (XI) was prepared according to Roberts *et al*⁹⁶ by slowly adding 12.0 g (0.119 mol) of triethylamine and 12.0 g of ethylchlorocarbonate to a solution of 10.0 g (0.115 mol) of *cyclopropanecarboxylic acid* in 100 ml of chloroform. After standing at room temperature for two hours the reaction mixture was cooled and 40 ml of anhydrous dimethylamine was bubbled into the solution. After one day the solvent was reduced by evaporation and 10 ml of water was added. The water phase was washed with chloroform many times and the combined chloroform extracts were dried. Vacuum distillation at 104-106°/30 mm Hg gave 10 g (75 %) of a colourless liquid. The NMR spectrum showed groups of complex signals due to the AA'BB'C spin system of the *cyclopropyl* protons around $\delta = 1.7$ (1 H), $\delta = 0.9$ (2 H) and $\delta = 0.7$ (2 H) in *ortho*-di-chlorobenzene.

N,N-Dimethylcyclopropanecarbothioamide (XII) was prepared by dissolving 12.4 g of compound XI in 100 ml of toluene and adding 12.4 g of phosphorous pentasulphide. The reaction mixture was refluxed for three hours. The solution was

filtered and the solid residue extracted with boiling toluene. The combined toluene solutions were distilled in vacuum and at 136-138^o/22 mm Hg a yellow oil was obtained, which crystallized in the condenser. The product (1.4 g, 10 % yield) crystallized from toluene-heptane 1:1 at - 30^o as colourless prisms, m.p. 53.5-54^o. (Found: C 54.6; H 8.48; N 10.5; S 24.2. C₆H₁₁NS (129.23) requires C 55.8; H 8.58; N 10.8; S 24.8). The *cyclo*-propyl protons gave three groups of complex signals (AA'BB'C spin system) around δ = 1.8 (1 H), δ = 1.2 (2 H) and δ = 0.8 (2 H) in *ortho*-dichlorobenzene.

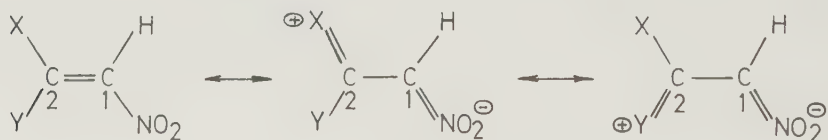
N,N-Dimethylisobutyramide (XIII) was prepared by refluxing 44.1 g (0.5 mol) of isobutyric acid and 60 g of thionylchloride for one hour. Distillation yielded 36.6 g of product at 85-95^oC. The acid chloride was slowly added to a cooled solution of 1 mol of dimethylamine in ethanol. After one day water was added and the reaction mixture was extracted with ether. The ether solutions were dried, and vacuum distillation gave 24.9 g of product at 90-92^o/40 mm Hg. Literature value: b.p. 175-176^oC⁹⁷.

N,N-Dimethylisobutyrrthioamide (XIV) was prepared by mixing 11.5 g of N,N-dimethylisobutyramide and 11.5 g of phosphorous pentasulphide in 60 ml of toluene and refluxing for one hour. The solution was filtered and the solid residue extracted with boiling toluene. The combined toluene solutions were distilled in vacuum. A yellow oil that crystallized when cooled to - 60^oC was collected at 114-119^oC/14 mm Hg. (Found: C 54.9; H 10.1; N 10.7; S 24.4. C₆H₁₃NS (131.24) requires C 54.9; H 10.0; N 10.7; S 24.4).

PART IV.

Substituted nitroethylenes.

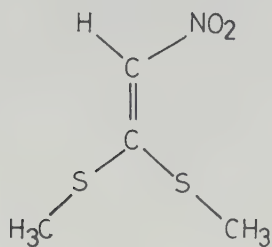
In ordinary ethylenes such as 1,2-dideuterioethylene the barrier to rotation around the carbon-carbon double bond is 60-65 kcal/mol⁹⁸. The introduction of electron-attracting substituents on one carbon atom and electron-donating substituents on the other leads to a considerable decrease of the barrier. The low barriers are due to the stabilization of the polar transition state, since a negative charge can be stabilized at the electron-attracting substituents and a positive one at the electron-donating substituents. The cis-trans conversion of *para*-amino-*para'*-nitrostilbene has been studied by Calvin and Alter⁹⁹, who obtained a ΔG^* of 30 kcal/mol at 100°C. Shvo *et al*¹⁰⁰ have measured low barriers to rotation around the carbon-carbon double bond in diacyl enamines. Sandström and Wennerbeck¹⁰¹ have studied different 1,1-bisalkylthioethylenes with carbon-carbon double bond barriers of a suitable magnitude for measurement on the NMR time scale, *i.e.* 18-25 kcal/mol. In 1-acyl-2,2-bisdimethylaminoethylenes, Sandström and Wennerbeck¹⁰² have found carbon-carbon double bond barriers of the order of 15 kcal/mol and lower.



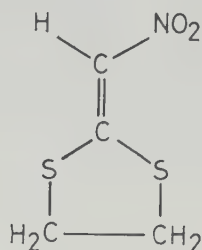
If the electron-attracting groups are large enough, and the dimethylamino groups are bound together to form a ring, the ethylene may be twisted in its ground state, as shown by Sandström and Wennerbeck¹⁰³.

When one or more of the electron-donating groups is an amine function, the carbon-nitrogen barrier can be measurable on the NMR time scale. Dahlquist¹⁰⁴ has determined the carbon-carbon double bond and the carbon-dimethylamino bond barriers in 1-cyano-1-carbethoxy-2-methyl-2-dimethylaminoethylenes.

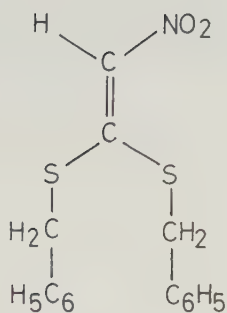
using a complete lineshape analysis. Manuschreck and Koelle¹⁰⁵ have measured the carbon-nitrogen barrier for 1-nitro-2-dimethylaminoethylene and for some other enamines.



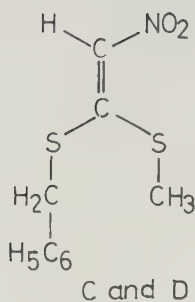
XV



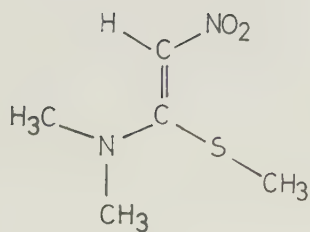
XVI



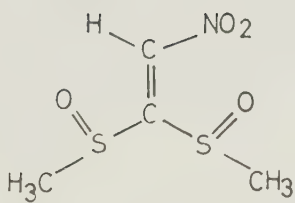
XVII



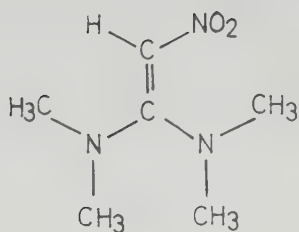
XVIII



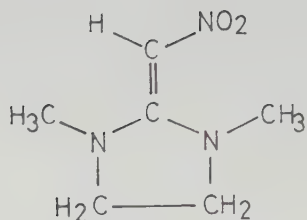
XIX



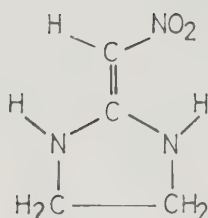
XX



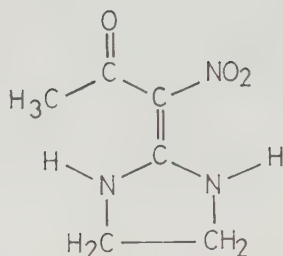
XXI



XXII



XXIII



XXIV

In this work the preparation of the molecules XV-XXIV is reported. To study the polarization of these systems, dipole moments for XV, XXI and XXII, and barriers for XVIII, XIX and XXI were measured.

Ultraviolet spectra of XV, XVI, XVII, XIX, XXII, XXIII, and XXIV were recorded.

Quantum chemical calculations with the PPP method were performed on systems corresponding to XV, XIX, and XXI.

Dipole moments.

The method of Hedestrand¹³ was used: for a more detailed description see page 11. 1-Nitro-2,2-bismethylthioethylene (XV) gave $a_e = 21.46$ and $a_n = 0.41$ from a least-squares plot of the data, leading to $\mu = 5.64 \pm 0.02$ D. 1-Nitro-2,2-bisdimethylaminoethylene (XXI) gave $a_e = 38.6$ and $a_n = 0.44$, from which $\mu = 7.46 \pm 0.01$ D was obtained. For 1,3-dimethyl-2-[nitromethylene]-imidazolidine (XXII) the dipole moment was determined in dilute solutions since the compound is poorly soluble in benzene. A check on compound XXI in dilute solution gave 7.47 D instead of 7.46 D. A least-squares plot of the data gave $a_e = 38.39$ and $a_n = 0.38$, which gives $\mu = 7.39$ D $\pm$ 0.05 for XXII.

Dipole moments can be subdivided into σ - and π -moments. The σ -moment can be estimated by vector addition of known group moments, calculated from non-conjugated compounds. The group moments were taken from Smyth¹⁰⁶, except that for the nitro group, which was calculated in the following way: PPP calculations, using the parameters mentioned below, gave a π -moment of 1.7 D. From the experimental dipole moment of nitromethane, 3.5 D¹⁰⁶, the σ -moment for the methyl group and the π -moment for the nitro group were subtracted giving a σ -moment of 1.4 for the nitro group. The dimethylamino group was assumed to be planar.

Vector addition of σ -moments gave 1.5 D for compound XV and 1.8 D for compound XXI.

PPP calculations gave a π -moment of 4.86 D for compound XV and 7.11 D for compound XXI. Vector addition gives 6.0 D for the total dipole moment of XV and 8.6 D for that of XXI. These values are quite close to the experimental values of 5.64 and 7.46 D, respectively.

NMR measurements.

In ref. 107 Isaksson, Sandström and Wennerbeck reported low barriers in polarized ethylenes. One of the compounds studied, 1-nitro-2,2-bismethylthioethylene (XV), shows only one resonance signal for the methylthio groups at room temperature in both deuteriochloroform and pyridine. The singlet splits to a doublet at lower temperatures, at 0°C in deuteriochloroform, and at - 5°C in pyridine. These observations were interpreted in terms of hindered rotation around the carbon-carbon double bond. A $\Delta G^\ddagger$ of 14.8 kcal/mol was calculated.

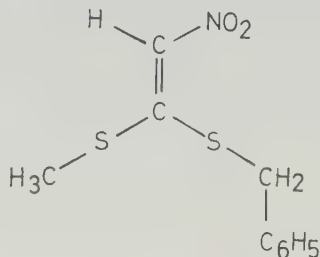
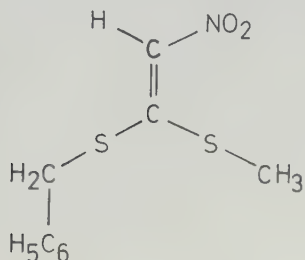
Later examination showed that the two methylthio groups gave two signals in benzene solution even when the temperature was raised to + 70°C, and in *ortho*-dichlorobenzene two signals even at + 171°C. The same behaviour was shown for the methylene signals in compound XVII.

Thus compound XV cannot have a particularly low barrier to rotation around the carbon-carbon double bond. The phenomenon was shown to be a temperature-dependent chemical shift. The singlet in deuteriochloroform begins to split to a doublet at + 59°C and in pyridine at + 98°C the singlet has split to a doublet with a shift of 1.6 Hz. The shifts of the methylthio groups are thus temperature-dependent in such a way that they pass each other at room temperature. This shows that great care must be taken when the non-exchanging shift is small. With a large non-exchanging shift, broadening of the signals at temperatures near the coalescence temperature is clearly visible, but with a small shift this typical feature is not easy to discover.

In order to determine the barrier around the carbon-carbon double bond the two isomers of 1-nitro-2-methylthio-2-benzylthioethylene (XVIII) C and D were prepared. In *ortho*-dichlorobenzene solution the methylene groups of the two isomers have different chemical shifts. The methyl groups also have different shifts, so the isomerization can be studied by observing the methylene groups as well as the methyl groups.

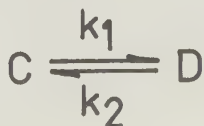
Isomer C is much more difficult to prepare than isomer D. Thus a study over a larger temperature interval was made with isomer D. At equilibrium the ratio of C to D is near unity throughout the temperature interval investigated.

The isomerization was followed on 60 mg of substance dissolved in 0.5 ml of *ortho*-dichlorobenzene. In this solution the resonance of the methyl group of C is at 128 Hz and that of D is at 124 Hz. The methylene signal of C occurs at 227 Hz and that of D at 240 Hz.



When the methylene proton signals were integrated, the temperature was measured before and after with the Varian ethylene glycol sample and when the methyl groups were integrated the temperature could be measured by means of an ethylene glycol capillary centered in the sample tube, then the temperature was measured before, during and after the integrations.

The isomerization is a reversible reaction and the



rate constants are obtained from

$$\ln \left(\frac{C_o - C_e}{C - C_e} \right) = (k_1 + k_2) t$$

The equilibrium constant $K = \frac{k_1}{k_2}$ was found to be unity, i.e. $k_1 = k_2$. Data are given in Table 15. Using equation 7 gives $\Delta S^\ddagger = -12 \pm 7$ e.u. and $\Delta H^\ddagger = 24.0 \pm 2.7$ kcal/mol.

The negative entropy of activation is in qualitative agreement with the negative entropies determined by Sandström and Wennerbeck¹⁰¹ in 1-benzylthio-2-methylthio-2-carbomethoxy-2-cyanoethylene in deuteriochloroform ($\Delta S^\ddagger = -24.0 \pm 2.9$ e.u.) and for 1,1-bismethylthio-2-benzoyl-2-cyanoethylene in *ortho*-dichlorobenzene ($\Delta S^\ddagger = -16.5 \pm 1.6$ e.u.). The negative entropies of the polarized ethylenes may be interpreted as showing that the transition state, which is more polarized than the ground state, is also more strongly solvated.

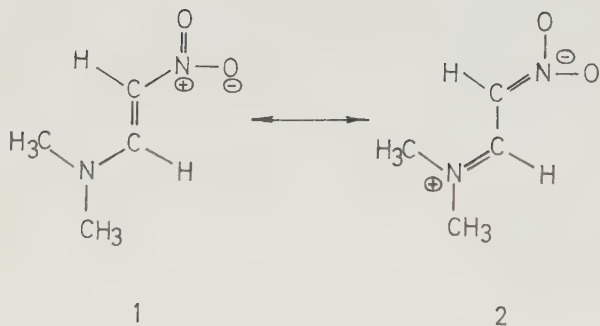
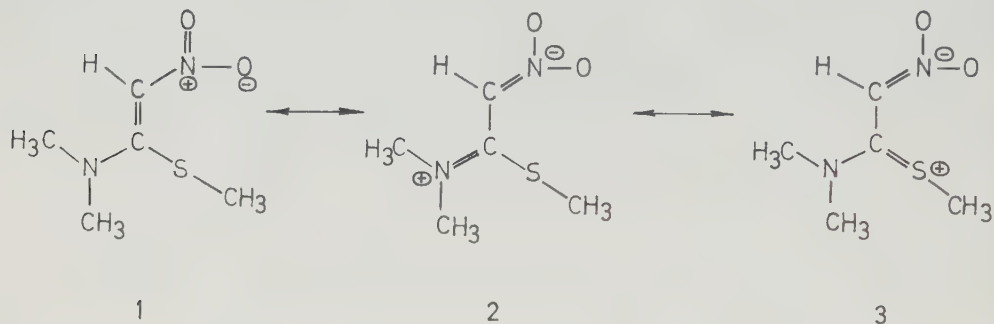
At room temperature, an NMR spectrum of 1-nitro-2-methylthio-2-dimethylaminoethylene (XIX) in deuteriochloroform gives one resonance signal at $\delta = 2.58$ assigned to the methylthio group and one at $\delta = 3.33$ assigned to the dimethylamino group. At -116°C the dimethylamino group gives a doublet with a chemical shift of 15.5 Hz, but the methylthio group still gives a singlet. At -103°C the doublet collapsed. Calculations using equations 3 and 6 give $\Delta G^\ddagger = 8.6$ kcal/mol at the collapse temperature. This has been interpreted as a carbon-nitrogen barrier. Two possible cases will be considered: a) the carbon-carbon double bond barrier is high and only one conformer is present; b) the carbon-carbon double bond barrier is extremely low and the two conformers interchange very rapidly. The observations may also be interpreted as a barrier around the carbon-carbon double bond, if the two methylthio signals below coalescence have the same chemical shift. A Varian HA-100 spectrometer was used. At low temperatures dichlorofluoromethane was the solvent. The temperature was measured with a methanol sample.

Mannschreck and Koelle¹⁰⁵ have found the carbon-nitrogen barrier in 1,1-dicyano-2-dimethylaminoethylene in deuterio-bromoform to be 18.0 kcal/mol ($\Delta G^\ddagger$), and Sandström and Wennerbeck¹⁰⁸ found that in 1,1-dicyano-2-methylthio-2-dimethylaminoethylene in deuteriochloroform to be 11.4 kcal/mol. The

Table 15.

Isomer	experiment	T °C	$\Delta G^\ddagger$ kcal/mol	mean lifetime in sec.	apparatus	integrated protons
C	a	102	28.0	1417	A 60	methylene
C	b	92	27.7	2500	A 60	methylene
D	c	95	28.3	4348	XL 100	methylene
D	d	90.9	28.5	8225	XL 100	methyl
D	e	97.5	28.4	3737	XL 100	methyl
D	f	109.0	28.7	1593	A 60	methyl
D	g	91.4	28.2	5483	A 60	methyl
D	h	84.9	28.4	15152	A 60	methyl

carbon-nitrogen barrier in 1-nitro-2-dimethylaminoethylene was determined by Mannschreck and Koelle¹⁰⁵ to be 16.5 kcal/mol. In the cases with two cyano groups at carbon atom 1 there is no doubt that the barriers measured are around carbon-nitrogen bonds. When hydrogen is substituted by a methylthio group the barrier is lowered by 6.6 kcal/mol, since the methylthio group



competes with the dimethylamino group for conjugation with the nitro group.

The barrier of 8.6 kcal/mol in 1-nitro-2-dimethylamino-2-methylthioethylene is certainly around a carbon-nitrogen bond since the same large barrier-lowering effect, from 16.5 kcal/mol to 8.6 kcal/mol, is obtained when a hydrogen is substituted by a methylthio group. The conjugative ability of

the methylthio group, illustrated by resonance structure 3, is apparently considerable.

At room temperature the four methyl groups in 1-nitro-2,2-bisdimethylaminoethylene (XXI) give one resonance signal. At -88°C the signal is 10 Hz broad. Spectra taken at lower temperatures indicate that both the carbon-carbon double bond barrier and the carbon-nitrogen barrier give rise to coalescences at -88°C . At -108°C the rather broad signal consists of four partially unresolved peaks. A rough estimate of the barrier around the carbon-carbon double bond is a $\Delta G^{\ddagger}$ of 9.7 kcal/mol and the barrier around the carbon-nitrogen bond is 10.0 kcal/mol. Dichlorofluoromethane was used as solvent.

Table 16. The shifts of the vinyl protons in deuteriochloroform.

Compound	δ
XV	7.12
XIX	6.80
XXII	6.38
XXI	6.32

Discussion.

Since there can be no change in anisotropy in the neighbourhood of the vinyl protons of the molecules listed in Table 16, the shifts provide valuable information about the electron densities at carbon atom 1.

The most polarized of the ethylenes examined here is XXI, the open diamino compound. The resonance of its vinyl proton is at highest field, $\delta = 6.32$, the dipole moment is 7.46 D and the barrier around the carbon-carbon double bond is 9.7 kcal/mol.

When the dimethylamino groups are bound together to form a ring as in compound XXII, the conjugation with the nitro group is not as effective as when the dimethylamino groups are free to rotate. The resonance of the vinyl proton of XXII comes at $\delta = 6.38$ and the dipole moment is 7.39 D. Dreiding models show that the nitro group and the nearest N-methyl group interfere with each other. When the dimethylamino groups are bound together to form a ring, this interference leads to a twist of the ring out of the planar conjugated system. In the open diamino compound only one of the dimethylamino groups must twist in order to avoid interference with the nitro group, and the other can conjugate to full capacity. The carbon-carbon double bond barriers in XV and XVIII are considered equal, *viz.* $\Delta G^\ddagger = 28.4$ kcal/mol. The resonance for the vinyl proton of XV is at $\delta = 7.12$ and the dipole moment is 5.64 D. The difference in chemical shifts of the vinyl protons and the dipole moments of XXI, XXII and XV reflect the fact that the methylthio group is inferior to the dimethylamino group in conjugating capacity.

The carbon-carbon double bond barrier in 1-nitro-2-methylthio-2-dimethylaminoethylene (XIX) was not measurable. The resonance of the vinyl proton is at $\delta = 6.80$. Since the electron distribution seems to be reflected in the vinyl proton shift and the $\Delta G^\ddagger$ is also dependent upon the electron distribution, it was worthwhile to correlate the $\Delta G^\ddagger$ and the vinyl proton shift in order to obtain at least a crude estimate of the carbon-carbon double bond barrier of XIX. By plotting the chemical shifts of the vinyl protons of XV and XXI *vs.* $\Delta G^\ddagger$ for XV and XXI an approximate $\Delta G^\ddagger$ of 21 kcal/mol for the barrier around the double bond of XIX was obtained. Most likely XIX exists in one conformer with the dimethylamino group furthest away from the nitro group.

Ultraviolet spectra.

The ultraviolet spectra of compounds XV, XVI, XVII, XIX, XXI, XXII, XXIII and XXIV were recorded in both polar and nonpolar solvents; the data are listed in Table 17. They all show a band with a high ϵ -value above 310 nm, which is assigned to a $\pi \rightarrow \pi^*$ transition.

Table 17. Ultraviolet spectra.

Compound	$\lambda_{\max}$ nm	log ϵ	$\lambda_{\max}$ nm ^e	log ϵ
XV	335 ^a	4.12	291	3.78
			355	4.17
XVI	333 ^b	4.15	351	4.21
XVII	334 ^b	4.13	296	3.90
			358	4.17
XIX	348 ^a	4.09	370	4.28
XXI	333.5 ^a	4.21	345	4.33
XXII	332 ^c	4.19	333.5	4.22
XXIII	328 ^d	4.39	323.5	4.37
XXIV	255.5 ^d	4.12	254.5	4.15
	312 ^d	4.10	311	4.09

a) in heptane with 0.3 % methylene chloride

b) in heptane with 0.5 % methylene chloride

c) in heptane with 0.6 % methylene chloride

d) in methylene chloride solution

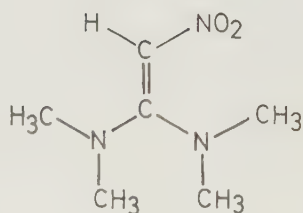
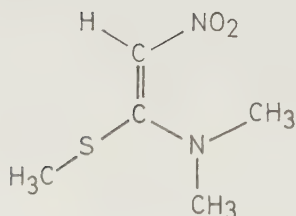
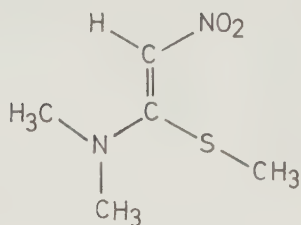
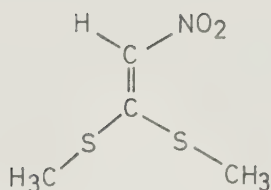
e) in ethanol

The ultraviolet spectrum of nitroethylene in the vapour phase has been recorded by Loos *et al*¹⁰⁹. A very strong band at 203 nm, a shoulder at 242 nm and a very weak band at 295 nm have been observed. The strong bands above 310 nm in the substituted nitroethylenes must come from conjugation through the whole molecule.

PPP calculations of the ultraviolet spectra have been performed on systems corresponding to XV, XIX and XXI. (See the following section).

PPP calculations.

Quantum chemical calculations were carried out on systems corresponding to the following molecules, using the PPP method:



The geometries were in part taken from Hess *et al*¹¹⁰, who determined the geometry of nitroethylene by microwave spectroscopy.

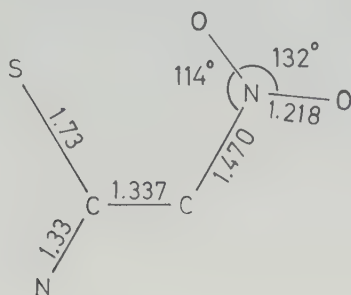


Fig. 13. Bond lengths and bond angles in XIX.

The angles at carbon atom 2 has been assumed to be 120° . The length of the C-S bond was chosen to be 1.73 Å which was obtained by X-ray crystallographic measurements on 1-cyano-1-*para*-bromo-phenyl-2,2-bismethylthioethylene¹¹¹. 1.33 Å was considered a good value for the C-N bond length, in accordance with crystallohraphic measurements on 1,3-dimethyl-2-[*para*-bromophenyl-cyano-methylene]-imidazoline¹¹¹.

The following parameters were used:

Table 18.

	$U_{\mu\mu}$ eV	$\gamma_{\mu\mu}$ eV	$\beta_{\mu\nu}$ eV
C- $\dot{\text{C}}$	-9.0	10.53	-2.92
C- $\ddot{\text{N}}$ _{nitro}	-24.80	12.27	-2.7
C- $\ddot{\text{N}}$ _{amino}	-23.13	12.98	-2.318
N- $\dot{\text{O}}$	-16.30	14.50	-3.05
C- $\ddot{\text{S}}$	-20.40	10.84	-1.159

Atomic core and one center repulsion integral parameters for the nitro group and the carbon atoms were taken from ref. 112 where Labhart and Wagnière report PPP calculations of the ultraviolet spectra and dipole moments of many substituted benzenes. Loos *et al*¹⁰⁹ used these parameters to calculate the ultraviolet spectrum of nitroethylene. They varied the β -value for the C-N_{nitro} bond to obtain good agreement between experimental and calculated data. The best fit was achieved with $\beta_{\text{CN}} = -0.4$.

All parameters for the amino nitrogen were taken from a paper by Fabian¹¹³, and the atomic core and one center repulsion integral parameters for sulphur were also from a work of Fabian¹¹⁴. The β -value for sulphur was that used by Jensen and Skancke¹¹⁵. The β -value for the C-N_{nitro} bond was varied between -3.0 and -0.6. The best agreement with experimental data was obtained with $\beta_{\text{CN}} = -2.7$. The results are given in Table 19. The ultraviolet spectrum of XIX, in which the $\pi \rightarrow \pi^*$ band appears of much longer wavelengths than in the case of XV and XXI, could not be reproduced in the PPP calculation. The first $\pi \rightarrow \pi^*$ transition for XIX in the calculations comes close to the first $\pi \rightarrow \pi^*$ transitions for XV and XXI.

Table 19.

	Experimental		Calculated	
	λ_{max} nm in nonpolar solvent	oscillator strength	λ_{max} nm	oscillator strength
XV	335	0.221	322.4	0.363
XIX with the amino group towards the nitro group	348	0.232	321.8	0.419
XIX with the methyl- thio group towards the nitro group	348	0.232	320.5	0.433
XXI	333.5	0.296	321.2	0.461

Preparative part.

The dipotassium salt of 1-nitro-2,2-bisthiolethylene (XXV) was prepared according to Gompper *et al*¹¹⁶. To a solution of 53.7 ml (1 mol) of nitromethane and 70 ml of carbon disulphide in 400 ml of abs. ethanol, a solution of 144 g of potassium hydroxide dissolved in 1 l of ethanol was added in portions. During the addition the temperature was kept at + 30 - 35°C. Brown crystals precipitated, yielding 186.2 g (87 %) of product. The crystals are labile and have detonated on several occasions.

1-Nitro-2,2-bismethylthioethylene (XV) was prepared according to Gompper *et al*¹¹⁶. To a solution of 64.0 g (0.3 mol) of XXV in 200 ml of water a solution of 50 ml of methyl iodide in 300 ml of ethanol was added. After one day, more water was added and crystals were obtained. Crystallization from ethanol yielded 33.2 g (68 %) of yellow crystals, m.p. 125°C. Literature value¹¹⁶ m.p. 125-126°C.

2-[Nitromethylene]-1,3-dithiacyclopentane (XVI) was prepared according to Gompper *et al*¹¹⁶, in analogy with the preparation of XV. Instead of methyl iodide, the corresponding amount of 1,2-dibromoethane in ethanol was added. Crystallization from ethanol gave a 68 % yield of yellow crystals with m.p. 109°C. Literature value¹¹⁶ m.p. 107-109°C.

1-Nitro-2,2-dibenzylthioethylene (XVII) was prepared by dissolving 8.56 g of XXV in 50 ml of water and adding a solution of 9.2 ml of benzyl chloride in 130 ml of ethanol. After one day brown crystals were obtained. Crystallization from toluene yielded 4.4 g (35 %) of yellow crystals, m.p. 110°C. (Found: C 60.5; H 4.46; N 4.54; S 20.3. $C_{16}H_{15}NO_2S_2$ (317.44) requires C 60.5; H 4.76; N 4.41; S 20.2).

1-Nitro-2-methylthio-2-benzylthioethylene (XVIII).

Isomer C.

4.26 g (0.02 mol) of XXV was dissolved in 20 ml of water and a solution of 1.23 ml of methyl iodide in 20 ml of ethanol was added. After 30 minutes crystals started to precipitate. They were filtered off and identified as XV. Immediately after the filtration, a solution of 2.3 ml of benzyl chloride in 60 ml of ethanol was added. The reaction mixture was allowed to stand at room temperature for one day, after which 0.9 g of yellow crystals was obtained. An NMR spectrum showed that the isomer ratio of C to D was 1:1.

This experiment was repeated several times and the isomer ratio was examined by NMR. Some of the experiments gave a larger portion of isomer C. By fractional crystallization from hexane, in which XVIII is slightly soluble, isomer C was obtained. At the boiling point of hexane (68°C) the isomerization is very slow. The best separation of the isomers was obtained when the crystallization was carried out in very dilute solutions. Isomer C crystallizes as needles, while isomer D crystallizes as plates. Glass rods were put into the warm solution and the needles were allowed to grow long for several days. The needles could very carefully be taken from the glass rod, while isomer D, which crystallized in plates, remained close to the rod. This separation was performed a couple of times until the per cent of D was diminished, after which a number of ordinary recrystallizations gave pure isomer C.

Isomer D.

8.56 g (0.04 mol) of XXV was dissolved in 40 ml of water and a solution of 2.4 ml of methyl iodide in 40 ml of ethanol was added. The crystals which precipitated after 30 minutes were filtered off and a solution of 4.6 ml of benzyl chloride in 100 ml of ethanol was added immediately after the filtration. The reaction mixture was allowed to stand for three days at room temperature. During this time the walls of the flask were rubbed occasionally. Brown crystals were obtained. Crystallization from hexane gave 0.2 g of yellow

crystals, which were found to be pure isomer D, m.p. 114.0 - 115.5°C.

1-Nitro-2-methylthio-2-dimethylaminoethylene (XIX) was prepared by dissolving 4.95 g (0.03 mol) of XV in 0.031 mol of dimethylamine in benzene. Benzene was added to make a total volume of 45 ml. The reaction mixture was refluxed for 25 minutes. According to thin layer chromatography some diamino compound (XXI) had formed and some starting material was left. The major part was apparently compound XIX. Evaporation gave sticky crystals that were dried on a potsherd. These crystals were chromatographed on silica gel and eluted by a mixture of 2-butanone and chloroform. The first fractions consisted of XV and the later fractions gave sticky crystals of XIX, which once again were dried on a potsherd. Repeated recrystallizations from ethyl acetate gave pure product. 0.3 g (6 %) of orange crystals was obtained, m.p. 59°C.

The time of refluxing is very critical. From a mixture of the three components XV, XIX and XXI compound XV always crystallizes. (Found: C 37.2; H 6.28; N 17.2; S 19.7. $C_5H_{10}N_2O_2S$ (162.22) requires C 37.0; H 6.21; N 17.3; S 19.8).

1-Nitro-2,2-bismethylsulfoxide-ethylene (XX) was prepared by dissolving 3.3 g (0.02 mol) of XV in 85 ml of acetone and adding 11 ml of perhydrole. After one day the solvent was evaporated, and crystals were obtained. Recrystallization from ethanol gave 0.41 g (11 %) of yellow plates, m.p. 175°C. (Found: C 24.6; H 3.74; N 6.95; S 33.1. $C_4H_7NO_4S_2$ (197.24) requires C 24.4; H 3.58; N 7.10; S 32.5).

1-Nitro-2,2-bisdimethylaminoethylene (XXI) was prepared by dissolving 4.95 g (0.03 mol) of XV in 30 ml of benzene and adding 0.12 mol of dimethylamine in benzene. The reaction mixture was allowed to stand for one day at room temperature, and the solvent was then evaporated. Crystals were obtained, which upon recrystallization twice from acetone yielded 2.4 g (50 %) of white-yellow crystals, m.p. 118°C. (Found: C 45.1; H 8.25; N 26.3; O 20.3. $C_6H_{13}N_3O_2$ (159.19) requires C 45.3; H 8.23; N 26.4; O 20.1).

1,3-Dimethyl-2-[nitromethylene]-imidazolidine (XXII)

was prepared by dissolving 16.5 g (0.1 mol) of XV in 300 ml of ethanol. 8.8 g of N,N'-dimethylethylenediamine was added and the reaction mixture was refluxed for 2 hours. Evaporation gave an oil that crystallized. After repeated recrystallizations from toluene, the pure product was obtained. The yield was 4.2 g (27 %) of light yellow crystals, m.p. 120-121°C. (Found: C 45.7; H 7.10; N 26.4; O 20.7. $C_6H_{11}N_3O_2$ (157.18) requires C 45.8; H 7.05; N 26.7; O 20.4).

2-[Nitromethylene]-imidazolidine (XXIII) was prepared according to Gompper *et al*¹¹⁶. 3.3 g (0.02 mol) of XV was dissolved in 100 ml of ethanol and 1.33 ml of ethylenediamine was added. The reaction mixture was refluxed for one hour, and on cooling yellow crystals formed. Recrystallization from ethanol gave 2.0 g (75 %) of white crystals, m.p. 174°C. Literature value¹¹⁶ m.p. 169-170°C.

2-[Acetylnitromethylene]-imidazolidine (XXIV) was prepared by dissolving 1.32 g (0.01 mol) of XXIII in 10.2 ml of acetic anhydride. The reaction mixture was heated to 105°C for one hour. After cooling, brown crystals were obtained, which after recrystallization from ethanol gave 0.21 g (13 %) of white crystals, m.p. 192°C. (Found: C 41.8; H 5.09; N 24.6; O 28.2. $C_6H_9N_3O_3$ (171.16) requires C 42.1; H 5.30; N 24.6; O 28.0).

REFERENCES.

1. Blackwood, J.E., Gladys, C.L., Loening, K.L., Petrarca, A.E. and Rush, J.E., J. Am. Chem. Soc. 90 (1968) 509.
2. Isaksson, G. and Sandström, J., Acta Chem. Scand. 24 (1970) 2565.
3. Isaksson, G. and Sandström, J., Acta Chem. Scand. 21 (1967) 1605.
4. Bloch, F., Phys. Rev. 76 (1946) 460.
5. Gutowsky, H.S., McCall, D.W. and Slichter, C.P., J. Chem. Phys. 21 (1953) 279.
6. McConnell, H.M., J. Chem. Phys. 28 (1958) 430.
7. Copyright 1965, Chandler, J.P., Physics Department, Indiana University.
8. Allerhand, A., Gutowsky, H.S., Jonas, J. and Meizner, R.A., J. Am. Chem. Soc. 88 (1966) 3185.
9. Drakenberg, T., Dahlquist, K. and Forsén, S., Acta Chem. Scand. 24 (1970) 694.
10. Rogers, H.T. and Woodbrey, J.C., J. Phys. Chem. 66 (1962) 540.
11. Glasstone, S., Laidler, K.J. and Eyring, H., "The Theory of Rate Processes", McGraw-Hill, New York, 1941, p. 190.
12. Van Geet, A.L., Anal. Chem. 40 (1968) 2227.
13. Hedestrand, G., Z. Physik. Chem. [B] 2 (1929) 428.
14. Janssen, M.J. and Sandström, J., Tetrahedron 20 (1964) 2339.
15. Wettermark, G., Tegnér, L. and Mårtensson, O., Arkiv Kemi 30 (1969) 185.
16. Nishimoto, K. and Mataga, N. Z. Physik. Chem. (Frankfurt) 13 (1957) 140.
17. Pople, J.A., Trans. Faraday Soc. 49 (1953) 1375.
18. Jensen, K.A. and Sandström, J., Acta Chem. Scand. 23 (1969) 1911.
19. Sandström, J., J. Phys. Chem. 71 (1967) 2318.
20. Zvonkova, Z.V., Astakhova, L.I. and Glushkova, V.P., Kristallografiya 5 (1960) 547; Chem. Abstr. 56 (1962) 12399.

21. Brown, B.T. and Katekar, G.F., Tetrahedron Letters 1969 , 23
22. Siddall, T.H., III and Stewart, W.E.,
J. Org. Chem. 32 (1967) 3261.
23. Walter, W., Maerten, G. and Rose, H.,
Ann. 691 (1966) 25.
24. Neuman, R.C., Roark, D.N. and Jonas, V.,
J. Am. Chem. Soc. 89 (1967) 3412.
25. Weil, J.A., Blum, A., Heiss, A.H. and Kinnaird, J.K.,
J. Chem. Phys. 46 (1967) 3132.
26. Jaffé, H.H., Chem. Rev. 53 (1953) 191.
27. McDaniel, D.H. and Brown, H.C.,
J. Org. Chem. 23 (1958) 420.
28. Jackman, L.M., Kavanagh, T.E. and Haddon, R.C.,
Organic Magnetic Resonance 1 (1969) 109.
29. Brown, I., Davis, T.D., Dostrovsky, I., Evans, O.I. and
Hughes, E.D., Nature 167 (1951) 987.
30. Janssen, M.J., Rec. Trav. Chim. 81 (1962) 650.
31. Walter, W., Schaumann, E. and Paulsen, H.,
Ann. 727 (1969) 61.
32. Janssen, M.J., Rec. Trav. Chim. 79 (1960) 454.
33. Rosengren, K.J., Acta Chem. Scand. 16 (1962) 2284.
34. Skulski, L. and Urbanski, T., Bull. Acad. Polon. Sci.,
Ser Sci. Chim. Geol., Geogr. 6 (1958) 293.
35. Skorygin, P.P. and Yegorova, L.S.,
Dokl. Akad. Nauk SSSR 121 (1958 D) 869.
36. Forbes, W.F. and Leckie, I.R.,
Can. J. Chem. 36 (1958) 1371.
37. Forbes, W.F., Mueller, W.A., Ralph, A.S. and
Templeton, J.F., Can. J. Chem. 35 (1957) 1049.
38. Grammaticakis, P., Bull. Soc. Chim. France [5] 18 (1951) 220
39. Burawoy, A. and Thompson, A.R.,
J. Chem. Soc. 56 (1956) 4314.
40. Latosh, N.I. and Pushkareva, L.V.,
Dokl. Akad. Nauk SSSR 124 (1958 G) 98.
41. Forbes, W.F. and Templeton, J.F.,
Can. J. Chem. 36 (1958) 180.

42. Carlin, R.B. and Wich, G.S.,
J. Am. Chem. Soc. 80 (1958) 4023.
43. Burgers, J. *et al.*, Rec. Trav. Chim. 77 (1958) 491.
44. Day, B.F., Campbell, T.W. and Coppinger, G.M.,
J. Am. Chem. Soc. 73 (1951) 4687.
45. Grammaticakis, P., Bull. Soc. Chim. France [5] 18 (1951) 534.
46. Anderson, L.C. and Steedly, Jr., J.W.,
J. Am. Chem. Soc. 76 (1954) 5144.
47. Russell, R.A. and Thompson, H.W.,
Spectrochim. Acta 8 (1956) 138.
48. Suzuki, J., Tsuboi, M., Shimanouchi, T., and Mizushima, S.,
Spectrochim. Acta 16 (1960) 470.
49. Siddall, T.H., III, Stewart, W.E. and Marston, A.L.,
J. Phys. Chem. 72 (1968) 2135.
50. Gosavi, R.K., Agarwala, V. and Rao, C.N.R.,
J. Am. Chem. Soc. 89 (1967) 235.
51. Walter, W. and Ruess, K.-P., Chem. Ber. 102 (1969) 2640.
52. Sandström, J. and Uppström, B.,
Acta Chem. Scand. 21 (1967) 2254.
53. Suzuki, J., Bull. Chem. Soc. Japan 35 (1962) 1456.
54. Rae, I.D., Can. J. Chem. 45 (1967) 1.
55. Walter, W., personal communication.
56. Johnson, C.E., Jr. and Bovey, F.A.,
J. Chem. Phys. 29 (1958) 1012.
57. Emsley, J.W., Feeney, J. and Sutcliffe, L.H.,
"High Resolution Nuclear Magnetic Resonance Spectroscopy",
Pergamon, Oxford 1965, Vol. 1, p. 595.
58. Rae, I.D., personal communication.
59. Pedersen, B.F., Acta Chem. Scand. 21 (1967) 1415.
60. Brown, C.J. and Corbridge, D.E.C.,
Acta Cryst. 21 (1966) 442.
61. Carter, R.E., Acta Chem. Scand. 21 (1967) 75.
62. Bertelli, D.J. and Gerig, J.T.,
Tetrahedron Letters 1967, 2481.
63. Harris, D.H. and Wellman, K., Tetrahedron Letters 1968, 5225.
64. Walter, W., Kubersky, H.P. and Ahlquist, D.,
Ann. 733 (1970) 170.

65. Kjellin, G. to be published.
66. Ho, P.-L., Yong, H.-C. and Fang, S.-N., Hua Hsüch Hsüch Pao 26 (1960) 1; Chem. Abstr. 55 (1961) 18635.
67. Ullman, F., Ann. 327 (1903) 113.
68. Kramer, H.E.A. and Gompper, R.,
Z. Physik. Chem. (Frankfurt) 43 (1964) 292.
69. Dahlquist, K. and Forsén, S.,
Acta Chem. Scand. 24 (1970) 2075.
70. Filleux-Blanchard, M.L., Clesse, F., Bignebat, J. and
Martin, G.J., Tetrahedron Letters 1969, 981.
71. Filleux-Blanchard, M.L., Durand, H. and Martin, G.J.,
Organic Magnetic Resonance 2 (1970) 539.
72. Dabrowski, J. and Kozerski, L.,
J. Chem. Soc. (B) 1971, 345.
73. Dabrowski, J. and Kamienska-Trela, K.,
Spectrochim. Acta 22 (1965) 211.
74. Drakenberg, T., Dahlquist, K. and Forsén, S. to be published.
75. Blanchard, M.L., Chevallier, A. and Martin, G.J.,
Tetrahedron Letters 1967, 5057.
76. Banwell, C.N. and Sheppard, N.,
Discuss. Faraday Soc. 34 (1962) 115.
77. Tsatsas, G., Bull. Soc. Chim. France [2] 14 (1947) 1011.
78. Flurry, R.L., Jr., "Molecular Orbital Theories of Bonding
in Organic Molecules", Marcel Dekker, Inc., New York 1968.
79. Mulliken, R.S., Rieke, C.A., Orloff, D. and Orloff, H.,
J. Chem. Phys. 17 (1949) 1248.
80. Binsch, G. In Eliel, E.L. and Allinger, N.L., "Topics in
Stereochemistry", Interscience, New York 1968, Vol. 3, p. 97.
81. Eilingsfeld, H., Seefelder, M. and Weidinger, H.,
Chem. Ber. 96 (1963) 2671.
82. Bignebat, J., Quiniou, H. and Lozac'h, N.,
Bull. Soc. Chim. France 1969, 127.
83. Klingsberg, E., J. Am. Chem. Soc. 83 (1967) 2934.
84. Hartmann, H., personal communication.
85. Hartmann, H. and Fabian, K., Patentschrift 74037 D.D.R.
86. Klayman, D.L. and Shine, R.J.,
J. Org. Chem. 34 (1969) 3549.

87. Fuson, N., Josien, M.L. and Shelton, E.M.,
J. Am. Chem. Soc. 76 (1954) 2526.
88. Rogers, M.T., J. Am. Chem. Soc. 69 (1947) 2544.
89. Rogers, M.T. and Roberts, J.D.,
J. Am. Chem. Soc. 68 (1946) 843.
90. Lukina, M.Yu., Russ. Chem. Rev. 31 (1962) 419.
91. Deno, N.C. In "Progress in Physical Organic Chemistry",
Interscience, New York 1964, Vol. 2, p. 148.
92. Carter, R.E., Márton, J. and Dahlquist, K.,
Acta Chem. Scand. 24 (1970) 195.
93. Bartell, L.S. and Guillory, J.P.,
J. Chem. Phys. 43 (1965) 647.
94. Skoda, W. and Schurz, J., Macromol. Chem. 29 (1959) 156.
95. Sandström, J., Acta Chem. Scand. 19 (1965) 2432 and earlier
papers.
96. Renk, E., Shafer, P.R., Graham, W.H., Mazur, R.H. and
Roberts, J.D., J. Am. Chem. Soc. 83 (1961) 1987.
97. Gabrilov, N.J., Koperina, A.V. and Klyuchareva, M.M.
Bull. Soc. Chim. France 12 (1945) 773.
98. Douglas, J.E., Rabinovitch, B.S. and Looney, F.S.,
J. Chem. Phys. 23 (1955) 315.
99. Calvin, M. and Alter, H.W., J. Chem. Phys. 19 (1951) 768.
100. Shvo, Y., Taylor, E.C. and Bartulin, J.,
Tetrahedron Letters 1967, 3259.
101. Sandström, J. and Wennerbeck, I.,
Acta Chem. Scand. 24 (1970) 1191.
102. Sandström, J. and Wennerbeck, I.,
Chem. Commun. 1969, 306.
103. Sandström, J. and Wennerbeck, I.,
Chem. Commun. 1971, 1088.
104. Dahlquist, K., Acta Chem. Scand. 24 (1970) 1941.
105. Mannschreck, A. and Koelle, V.,
Tetrahedron Letters 1967, 863.
106. Smyth, C.P. "Dielectric Behavior and Structure",
McGraw-Hill, New York 1955.
107. Isaksson, G., Sandström, J. and Wennerbeck, I.,
Tetrahedron Letters 1967, 2233.

108. Sandström, J. and Wennerbeck, I. to be published.
109. Loos, K.R., Wild, V.P. and Günthard, Hs.H.,
Spectrochim. Acta 25 (1969) 275.
110. Hess, H.D., Bander, A. and Günthard, Hs.H.,
J. Mol. Spectr. 22 (1967) 208.
111. Sandström, J., Liljefors, T., Abrahamsson, S. and
Rehnberg, G. to be published.
112. Labhart, H. and Wagnière, G.,
Helv. Chim. Acta 46 (1963) 1314.
113. Fabian, J., Theor. Chim. Acta 12 (1968) 200.
114. Fabian, J., Theor. Chim. Acta 9 (1967) 140.
115. Jensen, H. and Skanke, P.N.,
Acta Chem. Scand. 22 (1968) 2899.
116. Gompper, R. and Schaefer, P.N.,
Chem. Ber. 100 (1967) 591.

